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The Crystal Structure of Cyanuric Triazide[1]

EDWARD W. HUGHES, *Cornell University*

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Hexagonal cyanuric triazide has been examined by means of Laue, rotation and oscillation photographs and by a few spectrometer measurements. The dimensions are $a=8.70$A and $c=5.98$A. The space group is $H6_3/m$. There are two $C_3N_3(N_3)_3$ in the cell. The ten parameters have been determined by a qualitative Fourier analysis and the dimensions and angles of the molecule are given.

ALTHOUGH the azide group has been known to chemists for half a century its structure has long been in doubt. It is only recently through the electron diffraction studies of Brockway and Pauling[2] and dipole moment measurements of Sidgwick, L. E. Sutton and Thomas[3] that convincing results have been obtained regarding the structure of this important radical as it exists in organic compounds. It was the purpose of this investigation to confirm by the more orthodox methods of x-ray crystal analysis the structure found by electron diffraction. Because of its comparatively high symmetry and relatively simple chemical composition, hexagonal cyanuric triazide, $C_3N_3(N_3)_3$, was chosen for investigation.

The material used was prepared by the action of aqueous sodium azide upon cyanuric tribromide. The resulting triazide was recrystallized several times from purified acetone. Fragments of the crystals used melted at 93.5°C (corr.). The needles obtained were first order hexagonal prisms terminated by first order pyramids and were a half to three-quarters of a millimeter in thickness. Segments not over a millimeter long were used in all the x-ray examinations.

The length of the c axis was taken from spectrometer measurements of the reflections from the basal plane. Rotation pictures about the a and c axes were used to determine the length of a and to check that of c. Both dimensions were checked in the usual way by two Laue photographs taken with x-rays in one nearly parallel to c and in the other nearly normal to a $\{10\bar{1}0\}$ face. They are: $a=8.70$A and $c=5.98$A. With two molecules in such a cell the calculated density is 1.72 g/cc compared with T. C. Sutton's experimental value of 1.71 g/cc.[4]

The Laue picture taken with x-rays parallel to c shows only the symmetry of point group $6C_i$ and consequently the crystal may have the symmetry of point groups $6c$, $6C$ or $6C_i$. There are nine space groups based on these: $H3/m$, $H6$, $H6_1$, $H6_5$, $H6_2$, $H6_4$, $H6_3$, $H6/m$ and $H6_3/m$.

[1] This article is based upon a portion of a thesis presented by the author to the faculty of the Graduate School of Cornell University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] Brockway and Pauling, Proc. Nat. Acad. Sci. **19**, 860 (1933).

[3] Sidgwick, Sutton and Thomas, J. Chem. Soc. **1933**, 406.

[4] Sutton, Phil. Mag. **15**, 1001 (1933).

Reflections from (000 l) are observed for even l's only and this definitely eliminates $H6_1$, $H6_5$, $H6_2$ and $H6_4$. If the absence of odd orders of (0001) is a true space group suppression the space group must be $H6_3$ or $H6_3/m$. Since these differ only in z coordinates and varied evidence indicates that all z coordinates are zero or one-half, either space group can be used. Since the structure found is not polar, $H6_3/m$ has been assigned. The elements of symmetry of this space group have been indicated on Fig. 3.

The supposition that all z parameters are zero or one-half is strongly supported by two observations. First, if such be the case, for either space group the expression for the structure factors of general planes becomes

$$F_{hkl}=\sum_a f_a \operatorname{Cos} 2\pi(hx_a+ky_a) \quad \text{for } l \text{ even and}$$
$$F_{hkl}=\sum_a f_a \operatorname{Sin} 2\pi(hx_a+ky_a)$$

for l odd. This would require the reflections on different layer lines of rotation photographs about c to vary in intensity with h and k in the same way for all layer lines having the same kind of index, even or odd. Such is the case, as is shown in Fig. 1, which compares visual estimates of the intensities from two even and two odd layer lines. Secondly, the first three reflections from the basal plane were measured on a spectrometer. Relative integrated intensities were obtained. The relative structure factors derived from these are shown in Table I in comparison

TABLE I.

hkl	*F* (exp.)	*F* (calc.)
(00·2)	116.8	116.8
(00·4)	53.0	56.0
(00·6)	25.2	24.8

with structure factors calculated with all z coordinates taken as zero or one-half. The experimental values are on an arbitrary scale taken so as to agree with the calculated value for the (0002) reflection. The calculated values are based upon atomic form factor curves described more fully later.

Supposing that the molecule consists of a nearly hexagonal ring of alternately carbon and

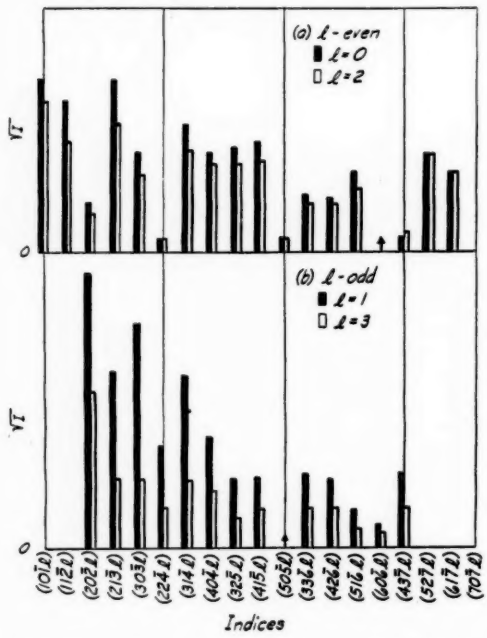

FIG. 1. Dependence of intensities upon h and k for even and odd values of l. Planes of the types $(hk\cdot l)$ and $(kh\cdot l)$ have not been separated. Arrows indicate the maximum possible intensities of unobservable reflections.

nitrogen atoms and that the azide groups are bound to the carbon atoms, we see that all atoms must be in the special position (h) of Wyckoff.[5] The parameters for this position are:

$$(\ x,\ \ y,\ 0\ )\ \ (y-x,\ -x,\ 0\ )\ \ (-y,x-y,\ 0\ )$$
$$(-x,\ -y,\ 1/2)\ \ (x-y,\ \ x,\ 1/2)\ \ (\ \ y,\ y-x,\ 1/2)$$

There will be five such positions occupied, one by carbon and four by nitrogen, and consequently there are ten x and y parameters to determine.

On the assumption that the azide group conforms to the model of Brockway and Pauling[2] and that the recent estimates of the other atomic radii by Sidgwick[6] are correct, models of the molecule were made and it was found possible to pack them together in layers having hexagonal symmetry and approximately the correct dimensions. These layers, one molecule thick, could be stacked on top of each other to give approximately the correct value of c in two ways,

[5] Wyckoff, *Analytical Expression of the Results of the Theory of Space Groups*, page 163, Carnegie Institution of Washington, Washington, D. C., 1930.

[6] Sidgwick, *The Covalent Link in Chemistry*, Cornell University Press, Ithaca, N. Y., 1933, Chapter III.

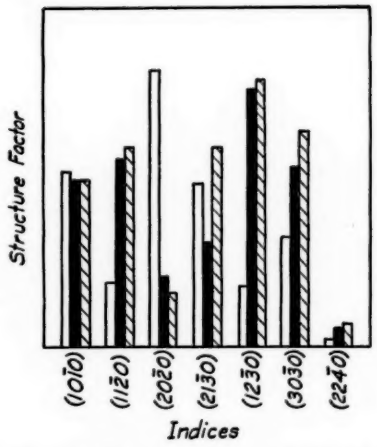

FIG. 2. Comparison of experimental structure factors (solid bars) with values calculated for structure I (open bars) and structure II (shaded bars).

I, with the cyanuric rings centered on the six-fold screw axis of the crystal, and II, with them centered on the three-fold axis. Not enough was certain about the atomic sizes or the molecular shape to choose between the two on those grounds. The parameters from each model were adjusted by rotating the molecules about their own three-fold axes until the structure factors calculated from each for the (22$\bar{4}$0) reflection were very small. This reflection was observed to be very nearly zero, which is abnormal for a plane of such large spacing. The structure factors of the first six prism zone reflections were then calculated for each model and these are compared with experiment in Fig. 2. It will be seen that model II, with cyanuric rings centered on the crystal's three-fold axis, gives much better agreement. The experimental structure factors are calculated from visual estimates.

It has generally been considered that the labor of a Fourier analysis is not justified unless one possesses fairly accurate measurements of the intensities observed. In this case however it seemed that such a procedure would yield the best possible parameters with less labor than a strictly trial and error method. Accordingly, the intensities of reflections from the prism zone planes were estimated visually with assigned numerical values instead of the usual classification into groups. In making these estimates frequent comparisons were made with spots of known intensity on a similar photograph of a known crystal. An underexposed film was used along with an overexposed one to help bridge the wide gap between the strongest and the weakest reflections. These intensities were corrected for the polarization and the Lorentz factors but all other corrections were considered unwarranted. The square roots of these intensities were then used as amplitudes in a Fourier analysis, the phases of the components being determined from the trial and error structure arrived at as described above. Graphical methods were used extensively and it was found possible to make a complete contour map of the relative electron density in two days' time. After some of the doubtful phases had been corrected, the result reproduced in Fig. 3 was obtained. Although only sixty-six of the larger amplitudes were used and although these were derived from visual estimates only, the method must give a fairly good placement of atomic centers. It is not unduly sensitive to errors in amplitude and the errors in estimation are reduced in taking square roots. The smaller amplitudes omitted are chiefly of importance in determining the "shape" of the outer portions of the atoms. It will be observed that the peaks representing carbon atoms are about eight-tenths as large as those for the nitrogen atoms, in agreement with the relative atomic numbers of the two elements.

The parameters obtained were tested by using them to calculate the structure factors of planes reflecting upon the zero and first layer lines of oscillation pictures made about *c*. In making these calculations the atomic form factors for carbon were taken from the curve derived from graphite and used by Mrs. Lonsdale.[7] The values used for nitrogen were obtained by correcting the theoretical values of James and Brindley[8] by factors determined from a comparison of Mrs. Lonsdale's values for carbon with James and Brindley's theoretical values for carbon. This was thought to be the best approximation obtainable because both the cyanuric ring and the azide group are probably "resonance" structures similar to the benzene ring type of structure which conforms satisfactorily to the data of Mrs. Lonsdale. The calculated and ob-

[7] Lonsdale, Proc. Roy. Soc. **A123**, 494 (1929).
[8] James and Brindley, Zeits. f. Krist. **78**, 470 (1931).

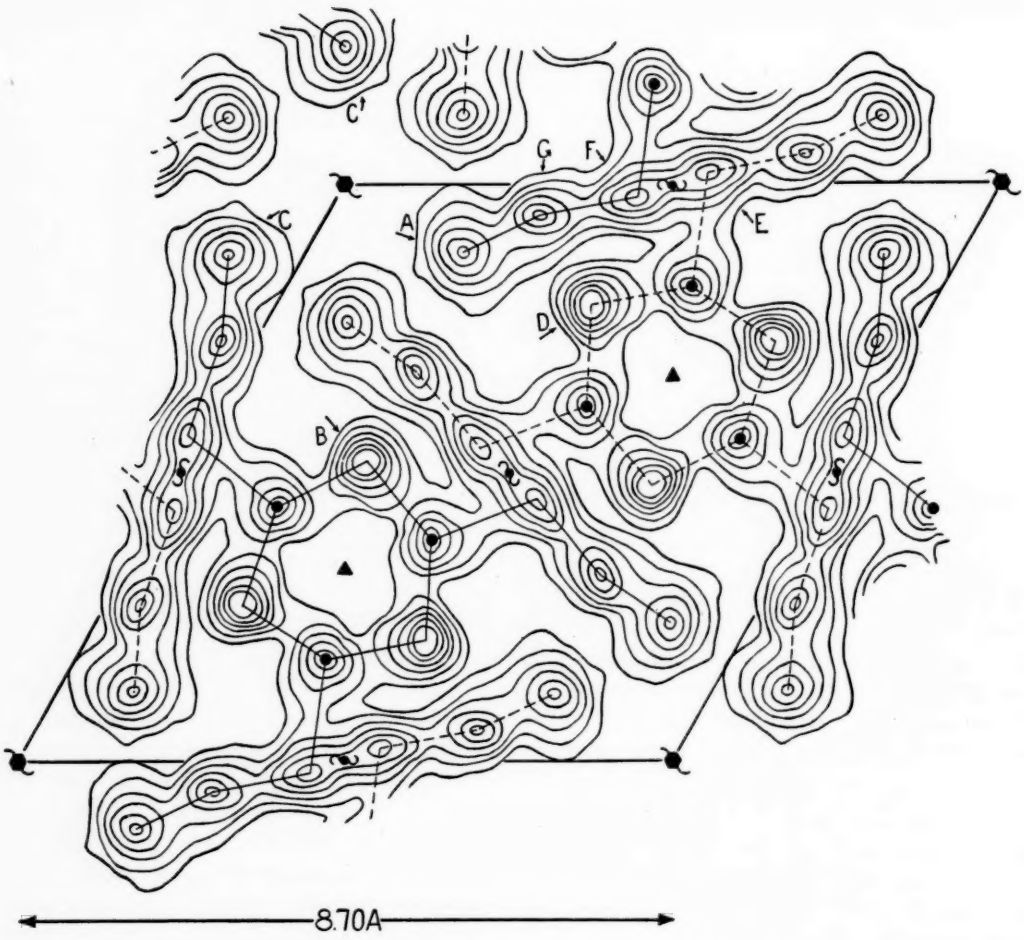

FIG. 3. Relative electron density projected on the basal plane. Black circles mark centers of carbon atoms. Atoms joined by solid lines have $z=0$ and 1. Those joined by broken lines have $z=\frac{1}{2}$.

served values are compared graphically in Fig. 4. The experimental values are on an arbitrary scale which was adjusted so as to give the best possible agreement for the whole range of values for $l=0$. The same scale was then maintained in the calculations for $l=1$. The maximum deviation noted is that for the reflection $(51\bar{6}0)$ and even if none of it is due to error in estimating the intensity it can be accounted for by an average error in the ten parameters of less than one-one hundredth of the unit cell length. As indicated on Fig. 1, intensities on the other layer lines vary with h and k in the same way as those on one or the other of the layer lines calculated and so must give as good agreement as they do. The parameters obtained are recorded in Table II.

TABLE II.

	C	N_I	N_{II}	N_{III}	N_{IV}
x	0.440	0.520	0.455	0.325	0.240
y	.615	.792	.022	.055	.115

The carbon to nitrogen distance in the cyanuric ring is 1.33A. These nitrogens are 1.43A from the center of the ring while the carbons are only 1.21A from the center. These carbon to nitrogen bonds make angles of 137° at the carbon atoms and 103° at the nitrogen atoms. The bond from carbon to azide nitrogen is 1.50A, or about 1.3 percent higher than the value given by Sidgwick.[6] This bond is not directed at the center of the cyanuric ring but is bent away from that direction by 2°. Such bending is inevitable in a tightly-

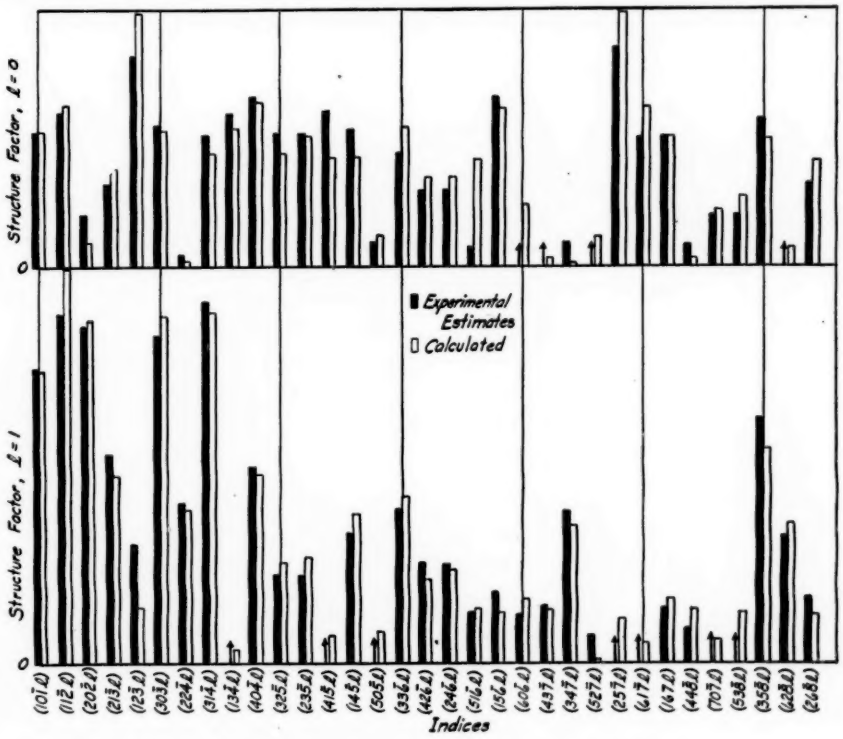

FIG. 4. Comparison of experimental and calculated structure factors. Arrows indicate the maximum possible structure factors for unobservable reflections.

packed structure. The azide group is not exactly linear but is bent 15° at the middle nitrogen. The distance of the nitrogen bound to carbon from the middle nitrogen is 1.29A and the distance from the latter to the terminal nitrogen is 1.09A. The first distance is 2.4 percent higher than the corresponding value of Brockway and Pauling while the latter is practically identical with their value. The angle between the carbon-azide bond and the first azide bond is 109°, much lower than Brockway and Pauling's corresponding value of 135°±15° for methyl azide.

The principal deviations from the azide structure found by Brockway and Pauling consist of this angle and in the bending of the azide group at the center. Both effects seem to be the result of crowding by neighboring molecules. The distances between the nitrogen centers indicated by letters on Fig. 3 are: *A* to *B* 3.04A, *A* to *C* and *C* to *C* 3.12A, *E* to *F* 3.15A and *D* to *G* 3.27A. These are the points of closest approach between neighboring molecules. The pressures arising from these contacts would tend to distort a linear azide group like that found by Brockway and Pauling for gaseous methyl azide in the fashion observed here. The average nitrogen to nitrogen distance between atoms on different molecules is 3.17A.

The proposed structure is radically different from that derived for the same crystal by T. C. Sutton.[4] It is, however, in substantial agreement with the approximate structure proposed recently by W. H. Bragg.[9]

The author takes this opportunity to express his gratitude to Professor A. W. Browne and to Professor W. L. Bragg for their interest and advice and particularly to Professor C. C. Murdock who generously made his x-ray equipment available for this work and whose advice was invaluable.

[9] Bragg, Nature **134**, 138 (1934).

The Structure of Rhombic Sulphur

B. E. WARREN AND J. T. BURWELL, *Eastman Laboratory of Physics, Massachusetts Institute of Technology, Cambridge, Massachusetts*

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From rotation and oscillation photographs with Mo $K\alpha$, rhombic sulphur is found to have the following cell and space group; $a=10.48$A, $b=12.92$A, $c=24.55$A, $Z=128$, space group $V_h^{24}(Fddd)$. The structure contains S_8 molecules which are symmetrical puckered rings with S−S distance 2.12A and bond angle $\alpha=105°$. The atomic coordinates are determined by comparison of calculated amplitudes with visual intensity estimates from oscillation photographs. The relation of rhombic sulphur to the high temperature forms is discussed briefly.

INTRODUCTION

SULPHUR is one of the few common elements whose crystalline structure has not hitherto been determined. Below 96°C sulphur is stable in the orthorhombic form. The orthorhombic crystals* are readily obtained, either as natural occurrences or grown from CS_2 solution.

UNIT CELL AND SPACE GROUP

Rotation patterns were made with Mo $K\alpha$ radiation using a small crystal grown from CS_2 solution. The axial lengths obtained were as follows: $a=10.48$A, $b=12.92$A, $c=24.55$A, in good agreement with the results of previous workers.[1] With a value 2.04 for the density, the number of atoms in the unit cell is calculated to be 128. From a set of 15° oscillation photographs, indices were assigned to several hundred reflections. With no exceptions, the systematic vanishings indicated the space group $V_h^{24}(Fddd)$. In this space group the general position is 32-fold, and hence all the atoms may be in the general position. Four atoms in the general position would involve 12 parameters, and as this is too large a number of variables to be determined solely by cut and try, it is necessary to make use of further information in seeking a solution of the structure.

THE S_8 MOLECULE

Chemical evidence[2] suggests strongly the existence of an S_8 molecule in rhombic sulphur. From a Fourier integral analysis of the powder pattern of sulphur,[3] it was found that on the average each atom in sulphur has two nearest neighbors at a distance of roughly 2.35A. This would require that the structure contain either long chains or closed rings, and since there is nothing about the physical properties of sulphur to indicate long chains, the ring molecule is the more probable. The chemical evidence and the diffraction data, taken together, indicate an S_8 ring molecule.

Although the S−S distance determined from the powder pattern is somewhat approximate, it is nevertheless close enough to the S−S distance found in the trithionate group[4] to justify the assumption that the bonding in the S_8 molecule is essentially the same as the S−S−S bonding in the trithionate group. Accordingly we assume the interatomic distances and bond angles to be the same as those found by Zachariasen, namely S−S=2.15A and $\alpha=103°$. Assuming a symmetrical puckered ring, the dimensions of the molecule are readily calculated. The ring can be considered as made up of two squares, one turned 45° with respect to the other (see Fig. 1). The planes of the two squares are separated by 1.15A, and the side of the square is 3.38A.

* We are indebted to Professor C. Palache of Harvard University for several large sulphur crystals, and to Dr. H. Berman for selecting and preparing them.

[1] Mark and Wigner, Zeits. f. physik. Chemie **111**, 398 (1924). $a=10.61$A, $b=12.87$A, $c=24.56$A, $Z=128$, space group V_h^{24}.

[2] Ephraim, *Anorganische Chemie*. Steinkopff, Dresden and Leipzig, 1934.

[3] B. Warren and N. Gingrich, Phys. Rev. **46**, 368 (1934).

[4] W. H. Zachariasen, J. Chem. Phys. **2**, 109 (1934).

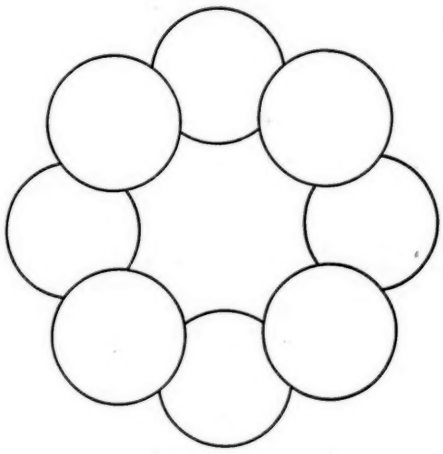

FIG. 1. S_8 Molecule in rhombic sulphur.

POSSIBLE ARRANGEMENTS

In the space group V_h^{24} there are 8-fold, 16-fold, and 32-fold positions, but since there are only 16 S_8 molecules in the unit cell, only the 8-fold and 16-fold positions come into consideration. With Wyckoff's notation,[5] the positions (*c*) and (*d*) can be immediately excluded as requiring centro-symmetry which the molecule does not possess. In the remaining positions there are nine major possibilities. A number of these can be ruled out immediately by intensity considerations, and others by the fact that atoms in neighboring molecules are brought closer together than is reasonable. The only likely possibility which remains is that involving 16g, with the rings located on the 2-fold axes parallel to *c*, the plane of the ring containing the *c* axis. Two parameters are still to be fixed, μ the position of the ring along the *c* axis, and φ the angle which the plane of the ring makes with the *a* axis.

The 00*l* spectra will involve only the parameter μ and this was determined by plotting the first six orders of 00*l* as a function of μ, and comparing with quantitative measurements of the integrated intensities obtained by measurements with an ionization spectrometer. The *hk*0 spectra will be independent of μ but will involve the parameter φ. A number of these reflections were plotted as a function of φ and compared with qualitative estimates of intensity from the oscillation patterns. In this way φ was determined to be about 50°.

From the approximate values of μ and φ determined in this way, the three coordinates of each of the four atoms in the general position were readily calculated. With these approximate coordinates the structure factors were calculated for about 60 planes. Comparing these calculated structure factors with the visual intensity estimates from oscillation photographs, small changes were made in the various coordinates until a generally satisfactory agreement was obtained. A rough but sufficiently good approximation to the Lorentz factor for oscillation photographs is obtained by setting

$$I \propto F^2/\xi,$$

where ξ is the coordinate of the reciprocal lattice[6] point in the equatorial plane, and F is the structure factor of the unit cell. A comparison of the calculated amplitudes $F/\xi^{\frac{1}{2}}$ with the observed intensity estimates is given in Table I. The general agreement is sufficiently good to verify the proposed structure.

The atomic coordinates are given in Table II. The origin of coordinates is at the intersection of three 2-fold axes, and the coordinates are given (a) in degrees, with 360° representing the

TABLE I. *Comparison of calculated amplitudes with observed intensity estimates.*

hkl	*F*	$F/\xi^{\frac{1}{2}}$	*I*	*hkl*	*F*	$F/\xi^{\frac{1}{2}}$	*I*	*hkl*	*F*	$F/\xi^{\frac{1}{2}}$	*I*
004	0	0	Nil	606	31	49	Nil	311	314	690	M.S
008	93	193	W.M	800	61	83	V.W	313	356	782	M.S
0012	0	0	Nil	804	97	132	V.W	315	51	112	Nil
0016	655	961	S	808	295	403	W.M.	317	376	825	M.S
0020	0	0	Nil	220	229	546	M	171	59	94	V.W
0024	520	623	M	222	602	1440	V.S	173	143	228	W
022	125	376	W	224	122	291	W	175	403	645	M.S
026	602	1810	V.S	242	141	276	W				
040	472	1010	S	244	298	583	MS.				
044	577	1230	S	246	29	57	Nil				
048	268	570	M	260	22	37	Nil				
062	610	1060	S	262	230	383	W.M				
066	216	375	W.M	264	60	100	V.W				
0610	188	327	W.M	440	56	95	V.W				
080	3	5	Nil	442	147	258	W				
084	95	143	Nil	444	225	381	W.M				
088	368	555	W.M	2100	90	119	W				
202	34	93	V.W	480	170	236	W				
206	440	1200	V.S	620	55	85	Nil				
400	338	652	M.S	660	740	1020	S				
404	242	467	M	6100	493	597	M				
408	427	824	M.S	840	52	68	Nil				
602	633	1000	S								

[5] R. W. G. Wyckoff, *The analytical expression of the results of the theory of space groups.*

[6] J. D. Bernal, Proc. Roy. Soc. (London) **A113**, 117 (1926).

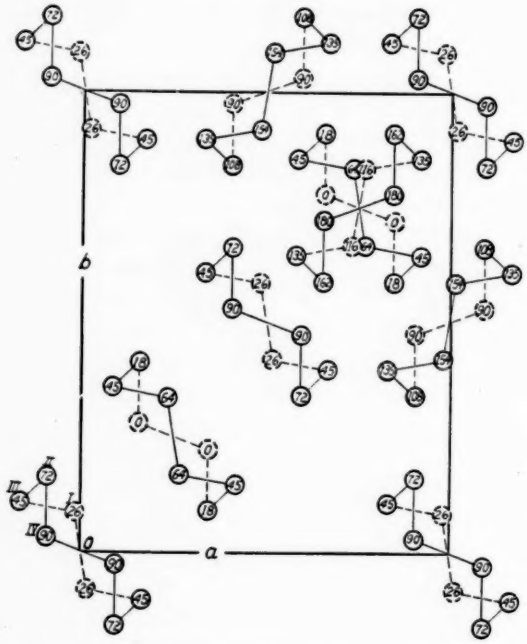

FIG. 2. Structure of rhombic sulphur. Only part of the molecules in the cell are shown, the "c" coordinates are given in degrees.

axial length, (b) as a fractional part of the axial length.

The complete structure is shown in Fig. 2. The c coordinates of the atoms are given in degrees, so that for example 90° means one-fourth of the c axis up from the plane of the paper. To avoid confusion, only part of the molecules in the cell are shown, in the lower left hand portion from 0–90°, and in the upper right hand portion from 0–180°.

The final values of the atomic coordinates were obtained by making small adjustments until a generally satisfactory agreement between calculated amplitudes and observed intensities was found. From these coordinates we can now calculate the S−S distances in the molecule and the bond angle. The results are given in Table III. As the coordinates were only fixed to the nearest degree they are uncertain by about 0.04A and hence the differences in the S−S distances in Table III probably have no significance.

TABLE II. *Atomic coordinates in rhombic sulphur.*

	θ_1	θ_2	θ_3	x	y	z
I	− 6	30	26	−0.017	0.083	0.072
II	−34	58	72	− .094	.161	.200
III	−60	38	45	− .167	.105	.125
IV	−34	10	90	− .094	.028	.250

TABLE III. *Interatomic distances and bond angles in S_8 molecule.*

S−S	Distance	Bond angles	
IV−IV	2.11A	I	105.0°
I−I	2.18	II	103.0°
IV−II	2.12	III	108.0°
II−III	2.11	IV	105.6°
III−I	2.07		
Aver.	2.12A	Aver.	105.4°

DISCUSSION

The structure of rhombic sulphur is definitely molecular. The S_8 molecule is a puckered 8 atom ring, with an S−S distance of 2.12A and bond angle of 105°. The closest distance of approach of atoms in neighboring molecules is about 3.3A. It is interesting to note that the molecules are arranged approximately in layers perpendicular to the c axis, with 4 molecules in each quarter of c. From the orientation of the molecules, the number of close neighbors which an atom in one layer has with atoms in the next layer is small, and hence the forces holding the layers together should be relatively weak. This is undoubtedly the reason for the very good c face cleavage.

Above 96°C rhombic sulphur changes over to a monoclinic form, and at 119°C the latter melts. Chemical evidence suggests that the molecule is still S_8 in both the monoclinic form and in the melt at temperatures not too far above the melting point. At about 200°C the limpid melt changes to a red highly viscous form. This is probably due to the S_8 rings breaking open, and forming irregular chains which tangle with one another and give rise to the marked increase in viscosity. Further study of the high temperature forms of sulphur is in progress.

Wave Mechanical Treatment of the Molecule Li_2^+

HUBERT M. JAMES, *Jefferson Physical Laboratory, Harvard University*

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The Li_2^+ molecule has been treated by methods previously applied to the study of Li_2 by the writer. It appears that the dissociation energy of Li_2^+ must be greater than that of Li_2, and is probably 1.30 ± 0.05 e.v. The ratio of one- to two-electron bond strengths appears to be greater with Li_2 than with H_2 because the bonding wave functions are more diffuse. The inner shells play a deterring role in the binding in Li_2^+ similar to that found in Li_2. The Heitler-London wave function has been compared with the much more accurate series function, and the general character of the satisfactory molecular orbital is noted. The form of the variational process used here appears to be particularly suitable for the treatment of one-electron bonds, and simple functions may be used to give highly satisfactory results, as illustrated by the cases of Li_2^+ and H_2^+.

I. INTRODUCTION

IN this paper it is proposed to extend to the discussion of Li_2^+, as a typical simple molecule involving a one-electron bond, the methods previously used by the writer in the treatment of the closely related molecule Li_2.[1] Though there seems to be no experimental data on this molecule, the lack of it is not a serious hindrance to the discussion, which is to be concerned principally with the more general questions of the value of the available methods for treating such molecules, the nature of satisfactory but simple molecular orbital functions, and the effect of the inner shells on the properties of the system. There is also internal evidence which may lead one to have considerable confidence in the quantitative significance of the results given by one method.

II. METHODS

For the quantitative treatment of molecules there are at present available four methods. Of these, the statistical method using the Fermi-Thomas field[2] is restricted in applicability to those cases in which the essential properties of the molecule are dependent on the presence of a fairly large number of electrons; it seems hardly worth while to apply it to so simple a system as Li_2^+, or indeed to any case in which there is a single bonding electron.

The Hund-Mulliken[3] method, that of representing the binding electrons by means of molecular orbitals constructed as linear combinations of atomic orbitals, gives in the case of Li_2^+ the same molecular function as the Heitler-London[4] method, as applied by Slater.[5] Using for the atomic orbitals functions of the type suggested by Slater,[6] one obtains in either case the wave function

$$\psi=\frac{1}{C}\begin{vmatrix} s(1\alpha,1) & s'(1\alpha,1) & s(1\beta,1) & s'(1\beta,1) & s(2\alpha,1)+s'(2\alpha,1) \\ s(1\alpha,2) & & & & \vdots \\ \vdots & & & & \vdots \\ \vdots & & & & \vdots \\ s(1\alpha,5) & \cdots & \cdots & \cdots & s(2\alpha,5)+s'(2\alpha,5) \end{vmatrix}.$$

Here $s(1\alpha,1)=[(2\delta_1)^3/4\pi\cdot 2!]^{\frac{1}{2}}e^{-\delta_1 r_1}\delta(\alpha/\sigma_1)$, $s(2\alpha,1)=[(2\delta_2)^5/4\pi 4!]^{\frac{1}{2}}r_1e^{-\delta_2 r_1}\delta(\alpha/\sigma_1)$,

r_1 being the distance from electron 1 to nucleus A, while $\delta(\alpha/\sigma_1)$ is the spin function and takes the values 1 or 0 as the spin of electron 1 is α or β. $s'(1\alpha,1)$ and $s'(2\alpha,1)$, respectively, have

[1] H. M. James, J. Chem. Phys. **2**, 794 (1934), hereafter referred to as I.
[2] F. Hund, Zeits. f. Physik **77**, 12 (1932).
[3] F. Hund, Zeits. f. Physik **73**, 1 (1931). R. S. Mulliken, Phys. Rev. **40**, 55 (1932), and subsequent papers.
[4] W. Heitler and F. London, Zeits. f. Physik **44**, 455 (1927).
[5] J. C. Slater, Phys. Rev. **38**, 1109 (1931).
[6] J. C. Slater, Phys. Rev. **36**, 57 (1930).

similar forms in terms of s_1, the distance from electron 1 to nucleus B.

Finally, one may apply the variational method, a particularly convenient form of which has been employed in the treatment of H_2[7] and Li_2. The wave function which has been used is $\psi=\sum_{m,\ j}C_{mj}\psi_{mj}$, where ψ_{mj} is like the unnormalized Heitler-London function, except that $s(2\alpha, 1)+s'(2\alpha, 1)$ is replaced by $f(mj\alpha, 1)$.

$$f(mj\alpha, 1)=e^{-(\gamma_2/2)\lambda_1}\lambda_1{}^m\mu_1{}^j\delta(\alpha/\sigma_1).$$

Here λ_1 and μ_1 are the elliptic coordinates of the electron in a coordinate system with the nuclei at the foci, and γ_2 is a parameter independent of m and j. Only terms with even j need be included in the series, since the wave function is known to be symmetric to reflection in the midplane between the nuclei. With a fixed value for γ_2, ψ is made the best available approximation to the correct wave function by so choosing the parameters C_{mj} as to make the energy associated with ψ a minimum. Thus, instead of representing the binding electron by the function $s(2\alpha, 1)+s'(2\alpha, 1)$ (known to be a good approximation for large separations of the atoms) one uses $\sum_{mj}C_{mj}f(mj\alpha, 1)$, which in practice may be made exceedingly flexible and resembles in form the known solutions of the $H_2{}^+$ problem for the internuclear distances which are of interest.

The methods used in working with these functions have been described in references 1 and 7. In fact, $J_{M_1J_1,\ M_2J_2}$ and $X_{M_1J_1,\ M_2J_2}$, as defined for the treatment of Li_2 in Eqs. (34) and (45) of the first of these papers, are the elements of the unity and energy matrices, respectively, needed for the variational treatment of $Li_2{}^+$. All the work necessary for the treatment of $Li_2{}^+$ by this method, except for the variation of the constants C_{mj}, was thus carried out in the normal course of the investigation of Li_2.

III. Results

The computations were all carried out for a single separation of the nuclei, chosen to be 2.98 atomic units (a.u.), principally because for this distance all the desired material was available from previous computations. This nuclear separation is 12 percent greater than that for which the minimum of the Li_2 potential curve is found, and may be expected to be approximately the equilibrium distance for $Li_2{}^+$.

1. Variational treatment

This computation was carried out with $\gamma_2=4$, a value chosen as probably suitable for Li_2. The computed values for the molecular energy were reduced to terms of binding energy by subtracting the energy of $Li+Li^+$, as computed by Wilson.[8] This energy is essentially the best which can be found for these atoms with the inner shell functions used in this work and a function for the outer electron which is independent of the position of the inner electrons; it is thus the lowest energy which could be given by a function of the character of our ψ when the nuclei are separated indefinitely.

The complete function was built up by adding one term at a time. The binding energy found after the addition of each term is given below in electron volts.

The first term was	ψ_{00},	giving	-0.49 e.v.
Add	ψ_{02}	to get	-1.116 e.v.,
then successively	ψ_{10}	to get	-1.143 e.v.,
	ψ_{04}		-1.195 e.v.,
	ψ_{12}		-1.221 e.v.,
	ψ_{20}		-1.242 e.v.,
	ψ_{22}		-1.242 e.v.,
and finally	ψ_{14}	to get	-1.243 e.v.

The improvement obtainable by adding terms involving higher powers of λ seems to be very small. Excluding terms with $j=4$, one obtains with the terms in λ^0 a binding energy of -1.116 e.v. Adding terms in λ depresses this by 0.043 e.v. to -1.159 e.v. Adding terms in λ^2 further lowers the result by 0.013 e.v. to -1.172 e.v. In view of the small importance of ψ_{14} it appears that one may expect a further improvement of only $\sim$0.005 e.v. from the indefinite continuation of this process. Similarly, the terms in μ^0 above gave a binding energy of -0.592 e.v. Addition of the terms in μ depresses this to -1.172 e.v., an improvement of 0.542 e.v., while further addition of μ^2 terms yields -1.243 e.v., down 0.071 e.v. It appears, then, that 0.03 e.v. would be a sufficient allowance for

[7] H. M. James and A. S. Coolidge, J. Chem. Phys. **1**, 825 (1933).

[8] E. B. Wilson, Jr., J. Chem. Phys. **1**, 210 (1933).

convergence in all directions, and that we may safely take -1.27 ± 0.02 as the limiting result.

The best six-term wave function was found to be $0.049274\psi_{00} - 0.087484\psi_{02} + 0.043777\psi_{10} + 0.051630\psi_{12} - 0.013152\psi_{20} - 0.069219\psi_{04}$, giving a binding energy of -1.242 e.v.

2. Heitler-London and related treatments

The Heitler-London treatment of Li_2^+ was carried through without other approximations than those inherent in the derivation of the wave function given above and the choice of δ_1 and δ_2 as 2.6875 and 0.672, respectively. These values were chosen for reasons given in I, the argument for the use of the relatively higher value of δ_2 being perhaps stronger for Li_2^+ than for Li_2. The binding energy found was -0.304 e.v., the energy taken for the separated atoms being that computed by using the limiting form of the molecular function, lying 0.047 e.v. above that obtained by Wilson.

Replacement of the complete Hamiltonian operator by the "interaction operator," as described in I, changed the computed binding energy by -0.014 e.v. With Li_2 at the same nuclear separation the result was a change of -0.032 e.v. in the binding energy. The approximate 1 : 2 ratio of these effects indicates the essential correctness of the assumption made in I, that the error associated with the use of this operator comes principally from the neglect of the overlapping of one atomic function with that part of the other where the electrons are likely to approach each other (i.e., for this case, the inner shell). Such an error would be reduced by 1/2 on removal of one of the outer electrons, while the error associated with the incorrectness of the outer electron function should almost vanish.

Omission of the inner shell functions further lowers the computed binding energy by 0.402 e.v. to -0.720 e.v. With this is to be compared the 0.587 e.v. found for Li_2 at this nuclear separation as the effect of the inner shells. As in that case, the important terms involving the inner shells may be associated with transitions of an electron from the outer shell of one atom to the inner shell of the other; their net effect is, however, rather larger than one would expect from a survey of the results with the neutral molecule.

IV. Discussion

The result of the variational treatment of Li_2^+ definitely indicates that the dissociation energy of the molecule is at least 1.25 e.v. Further, the situation is such that even more definite significance seems to be attached to the result. The essential coordinates which had to be omitted in the treatment of the problem were all associated with the inner shell electrons. The error in the convergence limit for the computed binding energy as a measure of the actual binding energy may then all be associated with the use of approximate inner shell functions and the neglect of polarization effects between the inner and outer electrons. Since both of these errors must be expected to be small[9] one may safely assume for this computation a higher degree of accuracy than was obtained with Li_2, and that the dissociation energy of Li_2^+ will differ essentially from 1.27 e.v. only as the equilibrium distance differs from 3A. Further, even if the computed point lies several tenths of an Angstrom unit from the minimum of the potential curve that minimum would lie only a few hundredths of an e.v. below the value found here. Thus one may confidently expect the dissociation energy of Li_2^+ to be 1.30 ± 0.05 e.v..

This value is somewhat greater than that for Li_2 (1.12 e.v.) contrary to the prediction of Pauling,[10] who, in the course of a discussion of the conditions for the stability of the one-electron bond, estimated that Li_2^+ would have a dissociation energy about two-thirds as great as that of Li_2. This estimate was made by reference to the situation with H_2^+ and H_2, considered to be analogous systems. It is thus of interest to see

[9] Computations on the Li atom by Dr. A. S. Coolidge and the writer, as yet unpublished, show that essentially the same ionization energy (to 0.01 e.v.) is found whether one employs the inner shell functions used in this work, or much more accurate ones. A similar lack of influence of the form of the inner shell functions on the computed binding energy is to be anticipated. Further, with Li the modification of the wave function to take account of polarization effects will increase the computed ionization energy by about 0.05 e.v. One may expect the importance of these effects to be somewhat greater in the molecule Li_2^+, where two inner shells are involved, but hardly by a factor of 2. Introduction of this further degree of flexibility into both atomic and molecular ion functions will thus probably increase the computed dissociation energy of Li_2^+, but by less than 0.05 e.v.

[10] L. Pauling, J. Am. Chem. Soc. **53**, 3225 (1931).

to what degree one can associate this unexpected result with the most obvious difference between the pairs of systems, the presence of inner shells in the one pair. The inner shells are apparently involved in the production of a repulsion; the observed binding may be considered to be the resultant of the binding of the outer electrons and this repulsive effect. Since the inner shell repulsion in Li_2 is greater than that in Li_2^+ the outer electron bonds, which may be taken as the proper quantities for comparison, are more nearly in the ratio 3 : 2 than are the total binding energies.

Taking for the inner shell repulsions the values obtained with the Heitler-London method, one gets for the outer electron binding -1.95 e.v. in the case of Li_2, -1.7 e.v. in the case of Li_2^+. Though the correction for the inner shells has thus improved the situation, it is still distinctly at variance with expectation. One can only bring the outer electron bond ratio to 3 : 2 by assuming that the Heitler-London method gives a marked underestimate of the inner shell repulsions, or that its behavior in the treatment of the two problems is very different. It seems most reasonable to assume that the Heitler-London method gives here, as elsewhere, an overestimate of repulsive effects. Taking this overestimate as one by 50 percent in the case of Li_2 (an assumption which was found to bring the Heitler-London treatments of H_2 and Li_2 into satisfactory parallelism) and by 100 percent in the case of Li_2^+ (since the method is less competent to deal with this problem), the outer electron binding is found to be -1.7 e.v. for Li_2, -1.5 e.v. for Li_2^+. It thus seems clear that with Li atoms the one-electron bond must be relatively stronger than with H atoms, even when inner shell effects are excluded. This may be associated with the greater diffuseness of the bonding electron function in the atom (weaker intraatomic forces associated with the $2s$ character of the electron), the perturbing forces in the ionic molecule causing a greater rearrangement of the charge density toward the center of the molecule, where it is effective in producing binding.[11]

In view of the relatively high ratio for the strengths of one- and two-electron bonds with Na and K atoms, and the probably smaller inner shell effect in the ionic molecules, one must expect Na_2^+ and K_2^+ to have higher dissociation energies than Na_2 and K_2, respectively.

As in the work on Li_2, the Heitler-London and Hund-Mulliken methods do not give acceptable results, the computed binding energy being less than one-fourth of that given by the variational method. There is, of course, little reason to expect these methods to be at all satisfactory when interatomic fields of the magnitude of those in Li_2^+ are present. Indeed, so poor an approximation is the Heitler-London function that each of two of the terms entering the series function is itself a distinctly better approximation to the correct function, ψ_{00} giving a binding energy of -0.49 e.v., ψ_{10} a binding energy of -0.57 e.v.

A comparison of the charge distributions associated with the Heitler-London and series functions is interesting in showing the way in which the first of these is inaccurate, and in indicating the general character of a satisfactory molecular orbital. By the use of the well-known property of determinants, that to any row (or column) any multiple of another row (or column) may be added without changing the value of the determinant, each wave function may be given the form

$$\psi=\frac{1}{\sqrt{5!}}\begin{vmatrix} f_1(1) & \cdots & f_5(1) \\ \cdot & & \cdot \\ \cdot & & \cdot \\ f_1(5) & \cdots & f_5(5) \end{vmatrix},$$

where f_n is normalized and orthogonal to all other f's. Integrating ψ^2 over the coordinates of electrons 2, 3, 4, 5, one obtains

$$\sum_{\text{spins}} \int \psi^2 dv_{2,\,3,\,4,\,5}=\tfrac{1}{5}(f_1^2(1)+f_2^2(1)+f_3^2(1)+f_4^2(1)+f_5^2(1))$$

as the chance of finding electron 1 at a given point in space, taking no account of its spin or the positions of the other electrons. That is, there is one chance in 5 of finding electron 1 in

[11] With H_2^+ at its equilibrium distance the Heitler-London method gives a charge density at the center of the molecule which is in error by a factor of less than 2, while at a corresponding distance in Li_2^+ the error is one of a factor of 4.

the charge distribution associated with each of the five orbitals. Just the same result must apply for each electron, and the charge density for the entire molecule is simply a superposition of the charge densities associated with the various orbitals. $\rho = f_1^2 + f_2^2 + f_3^2 + f_4^2 + f_5^2$. ρ is, of course, invariant to linear transformations of the f's which maintain their orthogonality, possessing a uniqueness of character which the f's lack.

Now, in the case under consideration the functions ψ and ψ' which are to be compared may be expressed in terms of four common f's, referring to the inner shells, and characteristic f's, which we call f_5 and f_5', respectively. The difference between ρ and ρ' is then precisely the difference between f_5^2 and $f_5'^2$. Further, each ρ is obtained by adding to the corresponding f_5^2 the charge distribution (to terms in $[\int s(1\alpha, 1)s'(1\alpha, 1)dv_1]^2$) of the two inner shells, treated separately. We are thus justified in considering the f_5^2's as being significant not only for a comparison of the ρ's, but also as indicating the nature of the molecular orbitals for the binding electron in each case.

In Table I will be found the values of the charge densities for the binding electron at various distances from the center of the molecule, measured along a line perpendicular to the internuclear axis, while in Table II are to be found similar values for points along the axis of the molecule. A nucleus is at the point 2.79 a.u. along this line. The sign (−) following a value indicates that it is the square of a negative value of f_5.

Perhaps the most striking difference in the charge distribution is to be found near the center of the molecule, where the charge density given by the Heitler-London function is only a fourth of that given by the series function. We observe with this latter function a considerably greater tendency for the charge to collect near the internuclear axis, between the nuclei. The Heitler-London function, on the other hand, places a considerable amount of charge on this axis outside of the nuclei, while the series function gives there a charge density which is exceedingly small. In the immediate neighborhood of the nuclei the Heitler-London function likewise gives much the larger density of charge, though the volume affected is so small that probably only a small fraction of the charge is involved in each case.

TABLE I. f_5^2 *at distance s from center of molecule along midaxial perpendicular.*

s (a.u.)	Series function	H.-L. function	s (a. u.)	Series function	H.-L. function
0	0.01397	0.00363	3.83	0.00098	0.00077
0.89	.01169	.00333	4.17	.00065	.00059
1.27	.00977	.00304	4.50	.00043	.00045
1.85	.00678	.00249	4.83	.00029	.00035
2.31	.00467	.00202	5.46	.00012	.00020
2.73	.00319	.00161	6.08	.00005	.00011
3.12	.00217	.00127	6.69	.00002	.00006
3.48	.00146	.00099			

TABLE II. f_5^2 *at distance s from center of molecule along nuclear axis.*

s (a.u.)	Series function	H.-L. function	s (a. u.)	Series function	H.-L. function
0	0.01397	0.00363	3.62	0.00080 (−)	0.00002
.27	.01383	.00361	3.90	.00012 (−)	.00068
.55	.01336	.00353	4.18	0	.00125
.83	.01247	.00336	4.46	.00001	.00150
1.11	.01099	.00301	4.74	.00002	.00151
1.39	.00873	.00237	5.02	.00004	.00140
1.67	.00560	.00133	5.30	.00004	.00123
1.95	.00194	.00016	5.58	.00004	.00104
2.23	.00006 (−)	.00124 (−)	6.14	.00003	.00070
2.51	.00965 (−)	.01708 (−)	6.69		.00045
2.79	.06884 (−)	.10540 (−)	7.25	.00001	.00028
3.07	.01655 (−)	.01776 (−)	7.81		.00016
3.34	.00385 (−)	.00163 (−)	8.37		.00010

It is the particular advantage of the form of the variational treatment we have used that the most effective factor in controlling the general character of the wave function is the exponential $e^{-\delta\lambda}$; it is thus especially suited for the construction of wave functions which concentrate the charge between the nuclei. It has been noted how a single term of this type which does not depend on μ, such as $\lambda^n e^{-\delta\lambda}$, can give relatively satisfactory results with Li_2^+. As a further example we may mention that with the function $\psi = ce^{-\delta\lambda}$ one obtains for H_2^+ with a nuclear separation of 2 a.u. (approximately the equilibrium distance) a binding energy of −2.16 e.v., in error by 0.62 e.v. This is a much more satisfactory result than that given by the Heitler-London method, and quite near the result of Finkelstein and Horowitz,[12] who varied the exponential parameter in a Heitler-London type function. Such a function, however, gives a charge density which is the same at all points on the axis between the nuclei, and is thus re-

[12] B. N. Finkelstein and G. E. Horowitz, Zeits. f. Physik **48**, 118 (1928).

stricted in its usefulness to relatively small internuclear distances.

The variation of the parameter δ is a very simple matter when only one electron is present, but in the more general case where one wishes to keep fixed the part of the function referring to other electrons it may be decidedly tedious. In such cases, in the absence of empirical rules or other information concerning the proper value of δ, it would probably be more convenient to use a series function involving several powers of λ, keeping δ fixed and varying the linear parameters. If it were then desired to reduce the function to a more simple analytical form, it could be plotted and fitted approximately with a single term having an appropriate δ.

A more satisfactory, but still very simple molecular orbital may be constructed by taking some account of the dependence of the function on μ, as well as λ. As noted above, a function of the form $e^{-\delta\lambda}(1+c\mu^2)$ has given with Li_2^+ a binding energy of -1.116 e.v., in satisfactory agreement with the limiting value of ~ -1.27 e.v., and this without any attempt having been made to vary δ. (It seems probable, however, that the choice of δ was a rather fortunate one.) With H_2^+ in the configuration considered above the corresponding result was a binding energy of -2.772 e.v., in error by only 0.005 e.v. This highly satisfactory result was obtained with the normalized function $e^{-1.35\lambda}(1.218+0.545\mu^2)$. Such a function is much more easily handled than the equally accurate one of Guillemin and Zener,[13] since it possesses only one exponential parameter, as compared with the two used by them. It is, of course, not so well adapted to the treatment of molecules for very large separations of the nuclei, but its range of applicability is obviously much greater than that of the function $ce^{-\delta\lambda}$. As in the case of that function, a variation of the parameter δ may be avoided by the introduction of terms in several powers of λ, followed by the fitting to the resulting function of a simpler one with δ properly adjusted.

This form of the variational method might be conveniently applied in conjunction with the statistical method of treating molecules,[14] and it possesses the advantage that one could avoid the use of an approximation to the statistical field in which an electron is to be considered as moving.

It is suggested that the function $\lambda^n e^{-\delta\lambda}(1+c_1\mu+c_2\mu^2)$ may be of general usefulness as a simple but satisfactory form for molecular orbitals when the atoms involved are of not too different size, and that a program for the determination of rules concerning the proper magnitude for δ would be of value. The use of orbitals of this form in molecular computations would be open to several objections which apply generally to computations with molecular orbitals—particularly that the wave functions tend to give too much importance to polar states of nonpolar molecules. This can be avoided only by the introduction and independent adjustment of terms in the function which depend on the position of two or more electrons, which will introduce an unsatisfactory but apparently unavoidable complexity into the treatment of molecules which do not have a particularly simple structure.

[13] V. Guillemin, Jr. and C. Zener, Proc. Nat. Acad. Sci. **15**, 314 (1929).

[14] A. Recknagel, Zeits. f. Physik **87**, 375 (1934).

On the Theory of Free Radicals and Organo-Alkali Compounds

BAILLI NILSEN, *Oslo, Norway*

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The theory of the free radicals of Pauling and Wheland is applied to the electron affinities of the radicals. The results are compared with the measurements of Bent, and they indicate that the charging electron enters in resonance with the whole system of $[p]_h$-electrons. The theory is generalized to unsaturated hydrocarbon radicals and it is shown that the formation of ionizable metal derivatives is due to the resonance between the charging electron and the $[p]_h$-electrons. Some cases of anomalous reactions of organo-alkali compounds are also interpreted.

E. HÜCKEL[1] as well as L. Pauling and G. W. Wheland[2] have proved that one can explain the dissociation of hydrocarbons in free radicals by a stabilization of the radicals. Earlier it was supposed that the dissociation was due to a weakening of the central C – C linking. This stabilization is caused by the resonance between the unpaired binding electron and the characteristic $[p]_h$-electrons* of the aromatic substituents. Using certain simplifications one can calculate the term-values according to the general methods and arrive at a satisfactory approximation to the experimental values of the heat and degree of dissociation.

As a further application of this theory it seems likely to try to explain some of the other characteristic properties of the triarylmethyl-complex. An inquiry into this question shows that it is impossible in this way to obtain a better understanding of the electron-affinities of such radicals.

In the quantum mechanical calculation of the e.a. of such a free radical one can imagine *a priori* two possible ways. One may suppose the problem solved for the free radical and then add the last electron in the same way as one does in the simplest cases. Or one can treat all electrons together, determining at first the term-value of the odd number of electrons which correspond to the free radical, and afterwards that of the even number corresponding to the negative ion, and equate the e.a. to the difference between the terms.

An investigation shows that the first method necessitates the introduction of rather arbitrary assumptions. The second method is closely related to that of Pauling and Wheland.[3] To obtain the coefficients of the exchange integrals these authors use a set of "canonical structures" containing one electron more than the free radical. Afterwards they omit the exchange integrals where the "phantom orbit" partakes of the exchange. In their other approximations they agree with Hückel. The question consists essentially in transferring in a reasonable way the approximations to the ionic problem. We must then remember that the "neighboring" electrons of the charging electron will not be the same ones in all structures, as we must suppose that the last one has the same initial wave function (with opposite spin) as the unpaired electron of the free radical. In a matrix element in the secular equation of the ion we therefore introduce the simple exchange integrals only where the charging electron is exchanged with its "partner" in the one or the other of the two structures of which the matrix element is formed. These will be "binding" exchange integrals. We shall suppose them to be equal to the other exchange integrals of neighboring electrons. This is only a rather rough approximation because the excess negative charge will probably weaken somewhat the exchange effect. On the other hand we thereby avoid the introducing of new

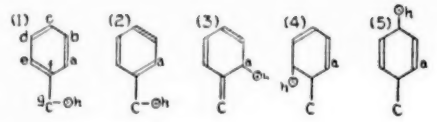
[1] Hückel, Zeits. f. Physik **83**, 632 (1933).
[2] Wheland, J. Chem. Phys. **1**, 362 (1933).
* Designation of Hückel. It means the electrons that cannot be placed in ordinary single bonds of an aromatic nucleus or of a double bond. H. supposes them to have wave functions with a node in the plane of the ring.

[3] See further: J. C. Slater, Phys. Rev. **38**, 1109 (1931); G. Rumer, Nachr. d. k. Ges. d. Wiss. zu Göttingen M. P. Klasse, p. 337 (1932); Pauling, J. Chem. Phys. **1**, 280 (1933).

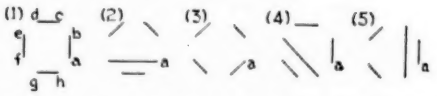
parameters which must be determined by the empirical data. In addition we make the strongly approximate assumption that the "non-binding" exchange integrals of the "charging" electron are negligible. At last we suppose the Coulombian integrals of the radical and of the ion to be equal.

As can easily be seen, all these approximations affect the result in the direction of lower term-value of the ion, and we must therefore expect the electron affinity obtained to be too large.

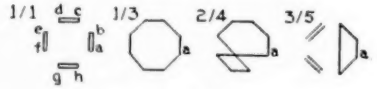
By the setting up and solving of the secular equation we proceed in the manner of Pauling and Wheland. To illustrate the method, we shall regard the case of the benzyl ion. Considering the following canonical structures:



with the corresponding schemes:



we get e.g. the following schemes of the matrix elements:



which give:

$$H_{1,1}=Q+ab+cd+ef+gh-1/2af-1/2bc-1/2de-1/2fg=Q+2\alpha$$
$$H_{1,3}=1/8Q+1/8(ab+af+bc+cd+de+ef+fg+ah+gh)=1/8Q+9/8\alpha$$
$$H_{2,4}=1/8Q+1/8(ab+af+bc+cd+de+ef+fg+eh+gh)=1/8Q+9/8\alpha$$
$$H_{3,5}=1/2Q+1/2(ab-1/2af+bc-1/2cd+de-1/2ef+fg+ah+ch)=1/2Q+9/4\alpha$$

where Q is the Coulombian integral and α the simple exchange integral. The secular equation will then be:

$$\begin{vmatrix} (Q-W)+2\alpha & 1/4(Q-W)+13/8\alpha & 1/8(Q-W)+9/8\alpha & 1/2(Q-W)+9/4\alpha & 1/4(Q-W)+3/2\alpha \\ 1/4(Q-W)+13/8\alpha & (Q-W)+2\alpha & 1/2(Q-W)+9/4\alpha & 1/8(Q-W)+9/8\alpha & 1/4(Q-W)+3/2\alpha \\ 1/8(Q-W)+9/8\alpha & 1/2(Q-W)+9/4\alpha & (Q-W)+2\alpha & 1/4(Q-W)+3/2\alpha & 1/2(Q-W)+9/4\alpha \\ 1/2(Q-W)+9/4\alpha & 1/8(Q-W)+9/8\alpha & 1/4(Q-W)+3/2\alpha & (Q-W)+2\alpha & 1/2(Q-W)+9/4\alpha \\ 1/4(Q-W)+3/2\alpha & 1/4(Q-W)+3/2\alpha & 1/2(Q-W)+9/4\alpha & 1/2(Q-W)+9/4\alpha & (Q-W)+2\alpha \end{vmatrix}=0.$$

Supposing that the structures 1 and 2 as well as 3, 4 and 5 enter into the linear combination with the same coefficients, the equation will be reduced to:

$$\begin{vmatrix} 5/2(Q-W)+29/4\alpha & 7/4(Q-W)+39/4\alpha \\ 7/4(Q-W)+39/4\alpha & 11/2(Q-W)+18\alpha \end{vmatrix}=0.$$

Hence

$$W=Q+3.8979\alpha,$$

and with

$$W'=Q+2.4091\alpha,$$

the e.a. will be

$$\Delta W=W'-W=+1.4887\alpha.$$

According to Pauling and Wheland we can obtain the coefficients of the Coulombian and exchange integrals in a matrix element of the reduced secular equation of a composed radical by means of the formulae:

$$\sum q=\sum q_1\sum q_2\sum q_3,$$
$$\sum a=\sum a_1\sum q_2\sum q_3+\sum q_1\sum a_2\sum q_3+\sum q_1\sum q_2\sum a_3,$$

where $\sum q_i$ is the coefficient of the Coulombian and $\sum a_i$ that of the exchange integral in the reduced secular equation of the simple radical $R_{(i)}-CH_2$. These rules can be used in the ionic problem too. We then get e.g. the reduced equation of the triphenylmethyl ion:

$$\begin{vmatrix} 125/8(Q-W)+2175/16\alpha & 343/64(Q-W)+5733/64\alpha \\ 343/64(Q-W)+5733/64\alpha & 1331/8(Q-W)+6531/4\alpha \end{vmatrix}=0,$$

$$W=Q+10.1445\alpha, \qquad \Delta W=-3.3362\alpha.$$

TABLE I.

		$-W$	V.e.	KgC.	V.e.
Benzyl	$C_6H_5CH_2$—	1.489	2.08		
α-naphthylmethyl	α-$C_{10}H_7CH_2$—	1.565	2.19		
β-naphthylmethyl	β-$C_{10}H_7CH_2$—	1.549	2.17		
Biphenylmethyl	$C_{12}H_9CH_2$—	1.564	2.18		
Diphenylmethyl	$(C_6H_5)_2CH$—	2.498	3.50		
Triphenylmethyl	$(C_6H_5)_3C$—	3.336	4.67	17.9	2.55±0.22
Diphenyl-α-naphthylmethyl	$(C_6H_5)_2$(α-$C_{10}H_7$)C—	4.299	6.02	18.6	
Diphenyl-biphenylmethyl	$(C_6H_5)_2(C_{12}H_9)C$—	4.271	5.98	19.1	
Phenyl-α-naphthyl-biphenylmethyl	(C_6H_5)(α-$C_{10}H_7$)$(C_{12}H_9)C$—	4.493	6.30	19.5	
Phenyl-dibiphenylmethyl	$(C_6H_5)(C_{12}H_9)_2C$—	4.430	6.20	19.8	
Tri-biphenylmethyl	$(C_{12}H_9)_3C$—	4.687	6.56	20.6	
α-naphthyl-dibiphenylmethyl	(α-$C_{10}H_7$)$(C_{12}H_9)_2C$—	4.679	6.55	20.2	
Diphenyl-β-naphthylmethyl	$(C_6H_5)_2$(β-$C_{10}H_7$)C—	3.932	5.50	18.6	

Treating in the same way α-naphthyl; β-naphthyl and biphenyl substituted methyl groups we find the values which are given in Table I. In the second column we have quoted the values of the e.a. putting $\alpha=1.4$ v.e. In the third column are given the e.a.'s measured by Bent and co-workers[4] for an ether solution; in the fourth the result for triphenylmethyl for the gaseous state. Bent has only calculated this value for the gaseous state, but accepting his own considerations the two values will provide a good basis for comparison.

We first note that the value for triphenylmethyl is too high, which is in agreement with our prediction. The difference, however, appears to be larger than might have been expected, since our calculations concern the normal state i.e., the absolute zero, while the measurements of Bent were carried out at a temperature $T=298°K$. For the other radicals the differences ought—according to the opinion of Bent—to be somewhat greater for the gaseous state than for the ether solution, in agreement with our theoretical expectations. It seems, however, as if the values for the radicals containing the α-naphthyl group turn somewhat out of the course of the empirical data, a circumstance for which we cannot give any plausible explanation, though it might perhaps be corrected by a slight improvement of the calculation method. It might in this connection be recalled that the α-naphthyl group shows a stronger dissociating influence upon hexa-aryl substituted ethanes than the β-naphthyl group.[5]

Whatever may be added to this point, the explanation of the relatively pronounced electron affinity of the free radicals (and of other special hydrocarbon-radicals (see below)) seems to lie in the fact that *the charging electron enters in resonance with the whole system of* $[p]_A$*-electrons.*

However, not only the free radicals but a good many other hydrocarbon-radicals are known to give alkali compounds of a similar character. All of these are characterized by unsaturation. We shall see that many of the affiliated questions obtain a reasonable solution when we consider them from our point of view. Some of these problems are already touched upon by Hückel[6] though he has not undertaken a more systematic investigation of the experimental material.[7]

We shall concentrate on types of compounds which are in the line with the free radicals, i.e., where the marked e.a. apparently is bound to certain carbon atoms substituted with unsaturated groups. This corresponds to the "reactive" or "acid methylene" of classical chemistry. Using this point of view we find that the predominant part of the phenomena—as can easily be seen—is attached to the methylene (or for three substituents methenyl-) groups of this sort.

By the method used here, one can first easily

[4] H. E. Bent, J. Am. Chem. Soc. **52**, 1498 (1930); **53**, 1780 (1931). Bent and M. Dorfman, J. Am. Chem. Soc. **54**, 1393 (1932).

[5] P. Walden, *Chemie der freien Radikale*, p. 296, Lpz. 1924.

[6] Zeits. f. Physik **70**, 204 (1931); **76**, 628 (1932).

[7] See the summaries of Wooster, Chem. Rev. **11**, 1 (1932); Schmidt, *Organometallverbindungen II*, Stuttg. 1934.

calculate the e.a. of a radical of the type $R-CH=CH-CH_2$ by supposing resonance between the structures:

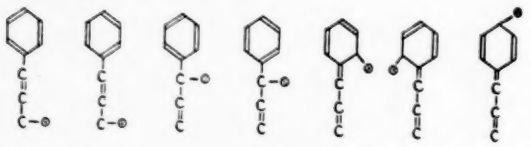
$$R-CH=CH-CH_2^{+} \text{ and } R-CH^{+}-CH=CH_2.$$

We then get the e.a.

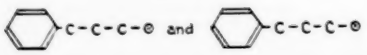
$$W=1{,}333\alpha.$$

For unsaturated radicals with a triple bond the problem is a good deal more complicated, as we do not know the electronic structure of such a bond. There is, however, every reason to suppose that at least one pair of the electrons of the bond is formed by $[p]_h$-electrons and can enter into resonance with the charging electron. Probably also a second one of the electron pairs is formed in a similar way and contributes to the resonance. The stronger electronegative effect[8] seems to support this assumption. The electronic structure of the triple carbon-carbon bond has, however, claim to a separate and broader investigation, as it has a good deal of chemical interest because of the peculiar metal compounds of the type $R-C\equiv C-Me$[1].

It is further—still under the point of view of the "acid methylene"—of interest to point out that the transmission of the effect of an aromatic nucleus through a double bond[9] is easily explained when we consider the possible structures of such a radical in comparison with the corresponding unsaturated radical. We can, e.g., for the cinnamyl-radical expect resonance between the following structures:



while the corresponding hydrocinnamyl-radical only permits resonance between:



We can now make similar considerations concerning more complicated substituents and show that similar circumstances must exist—not only in case of the previously treated aromatic nuclei—but also in case of longer chains of *conjugated* double bonds etc.

It might have been of interest to consider some more of the material concerning organo-alkali compounds from the point of view of "acid methylene," because some of those who have been occupied with the subject seem to have overlooked the close analogy between the aryl- and unsaturated- substituted "acid methylene" (and methenyl). By going over the material[7] one can, however, convince oneself of the role played by the aromatic and unsaturated substituents by the easy forming of alkali derivatives. One can further without difficulty see that the reactions have a pronounced tendency to be connected with just those carbon atoms which are substituted with such groups. We may then be content by establishing the following conclusion: With the exception of the acetylenides, *a smooth substitution or addition of alkali metal to a hydrocarbon with the forming of an easily ionizable (generally strongly colored) alkali compound will take place only at such places in the molecule where the embodied charging electron (s) can enter into resonance with the $[p]_h$-electrons of aromatic or unsaturated substituents.*

Hereby nothing is, of course, said about the places in the molecule where the reactions of the formed ion are connected; nor anything whether a substitution or an addition will be the reaction really taking place.

We have not yet touched the interesting question whether the supposed resonance between the different localizations of the charging electron has any direct chemical meaning. To examine this we recall the case of the benzyl ion. In that case—as in the other ones—we supposed the different structures (five) to be in resonance, and searched for the "right" linear combination $\psi=\Sigma c_i\psi_i$ of the wave functions ψ_i of the initial states. We found this by introducing the electron interaction and solving the corresponding secular equation. In the language of the statistical interpretation this means that there is some probability to find the charging electron at the ortho- and para-position in the nucleus. Supposing as before, the structures to be orthogonal and the ψ_i's normalized, we find in this case:

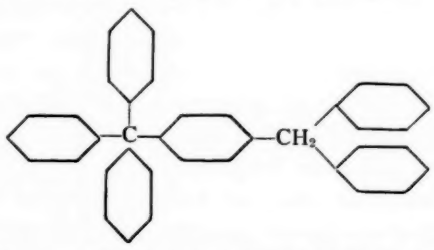
[8] L. Lapayre, Thèse, Lyon 1930.
[9] G. Wittig and M. Leo, Ber. **63**, 943 (1930); E. Bergmann, Ber. **63**, 2593 (1930); Wittig, Ber. **64**, 477 (1931); see also reference 8.

$$\psi = 0.20188(\psi_1+\psi_2)+0.1580(\psi_3+\psi_4+\psi_5).$$

The probability is then a finite one. We hence draw the conclusion, without making any assumption of the mechanism of the reactions, that one can expect some of the reactions of the ion to be connected with the para- and ortho-position.

We shall see that this conclusion is confirmed by certain—though few—anomalous reactions of the alkali compounds of benzyl and similar compounds. As a case of ortho-reaction may be mentioned that benzyl-sodium and-lithium with formaldehyde gives orthotolylalcohol.[10] The same product is obtained by treating benzylmagnesium-chloride with trioxymethylene. A para-reaction is, as far as we know, never found in the case of benzyl; the reaction of triphenylmethyl-sodium with triphenylacetyl-chloride, however, which gives *p*-benzhydryl-$\omega.\omega.'\omega.''$-triphenyl-acetophenone[11] is an example of such a reaction. In the same connection may be mentioned the polymerization of triphenylmethyl to *p*-benzhydryl-tetraphenylmethane with sodium as a catalyst.[12] That this reaction takes place with hydrogen chloride and even autocatalytically should not surprise us, as we ought to expect similar conditions in the case of the free radicals. A similar—though not so clear—case with an unsaturated radical we meet in cinnamylmagnesium-chloride which apparently reacts as $C_6H_5C(MgCl)=CH-CH_3$.[13] We must here suppose a secondary displacement of the double bond. The $\Delta^{\alpha,\beta}$-compound should be preferred from considerations of energy, on account of the conjugation of the double bond with the aromatic nucleus.

[10] Wooster, reference 7, p. 18, 32.
[11] Wooster, reference 7, p. 33.
[12] Walden, reference 5, p. 80 note.
The formula of *p*-benzhydryl-tetraphenylmethane is



[13] Gilman and Harris, J. Am. Chem. Soc. **53**, 3541 (1931).

An especially illuminating case of an anomalous reaction we find in the reactions

$$(C_6H_5)_2C=CH.CH(OCH_3)C_6H_5+K$$
and $$(C_6H_5)_2C(OCH_3).CH=CHC_6H_5+K,$$

which give identical metal compounds (yielding identical products by all chemical reactions). The same holds for the corresponding hydrocarbons (with H for OCH_3) by the action of phenylisopropyl-potassium.[14]

It will be shown by these few examples that the supposed resonance so far from contradicting the chemical facts, rather completes and explains them in a quite satisfactory manner.

Before finishing our considerations, we may mention a case which seems to fall somewhat outside the theory outlined here. The addition products of stilbene with lithium and sodium[15] yield by action of carbon dioxide, meso- *viz.* racemic diphenyl-succinic acid, a phenomenon which seems to be difficult to reconcile with the supposed resonance. It is however as Ch. B. Wooster[16] has pointed out, by no means excluded that there exists stereoisomerism between the ions formed. In our opinion the different color of the two addition products makes an assumption of different electronic structure obvious. At any rate there does not seem to be any reason to expect that a more thorough discussion of this exceptional case will entail any considerable revision of the theory outlined above.

An obvious further task of the above theory of free radicals is the interpretation of the positive "carbonium" ions. This problem seems to offer rather great difficulties. For the first, it seems as if the binding of the unpaired electron were entirely Coulombic in nature as, e.g., the benzyl radical only exceeds the positive benzylium ion with a minimum (0.0091α) resonance energy. Second, the substituents in the aromatic nuclei play a rather great role for the formation of a base, a fact that will complicate the quantum mechanical treatment a good deal. Nevertheless the task is enticing, inasmuch as one possibly could throw some light on the many interesting phenomena which are connected with the great and important group of triphenylmethane dyes.

[14] Wooster, reference 7, p. 55f.
[15] Wooster, reference 7, p. 27.
[16] Wooster, reference 7, p. 27f.

A Direct Experimental Determination of Electron Affinities, the Electron Affinity of Iodine

PAUL PORTER SUTTON* AND JOSEPH E. MAYER, *Chemical Laboratory of The Johns Hopkins University*

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By observing the ratio of the negative ion emission to the electron emission from a thermionic surface of known temperature in an atmosphere of electronegative molecules of known pressure the electron affinity of the atoms can be calculated. A magnetron set up has been used to distinguish electron and ion currents. With a tungsten filament at about 2000°K, and an iodine atmosphere of about 1 micron pressure, the electron affinity of iodine atoms has been found to be 72.4±1.5 kcal.

INTRODUCTION

THE measurement of the electron affinity of gaseous electronegative atoms has been for some time a problem of considerable interest, but no generally satisfactory method of attack has as yet been evolved. Attempts to observe the recombination spectra[1] or the absorption spectra limit of the free ions[2] have always failed due to the low intensities obtained.

Theoretical calculations[3, 4] and experimental measurements[5, 6] of the lattice energies of the alkali halides enable the calculation of the electron affinities of the halides, the results of which are undoubtedly of considerable accuracy, but this method is not only indirect but is also of limited applicability.

The method described here, and used on iodine, appears, with slight modifications to be of very general applicability. It is direct and simple. It is, however, subject to one difficulty of interpretation which detracts considerably from the certainty of the results. This point will be discussed at the end of this section.

The electron affinity of an atom is the negative of the energy change, ΔE_0 at absolute zero of the reaction (1),

$$X_{\text{gas}}+e^-_{\text{gas}}\rightarrow X^-_{\text{gas}}. \qquad (1)$$

The method presented here for measuring this quantity is based on the following considerations: Regard any surface in temperature equilibrium at a temperature T_s with a gas phase containing atoms, X, ions, X^- and electrons, e^-. Since equilibrium exists the numbers of each atom species, 'a,' striking unit surface per unit time from the gas phase must be equal to the numbers leaving the surface. The numbers striking, and therefore the numbers leaving, unit surface per unit time, Z_a, bear a simple relation (2) to the equilibrium pressure, P_a, in the gas phase and therefore to the equilibrium constant, K, and to the standard free energy change, ΔF, of reaction (1).

$$Z_a=P_a/(2\pi m_a kT_s)^{\frac{1}{2}}, \qquad (2)$$

$$K=e^{-\Delta F/RT_s}=\frac{P_{x^-}}{P_x\cdot P_{e^-}}=\frac{Z_{x^-}}{Z_x\cdot Z_{e^-}}(2\pi m_e kT_s)^{\frac{1}{2}}, \qquad (3)$$

where T_s = temperature of equilibrium, m_a = mass of particle "a," k = Boltzmann's constant.

Now if the reflection coefficient of the surface for each species is zero, that is, if each atom striking from the gas phase remains long enough on the surface so that its chance of leaving as an ion is the same as if it had been an ion when it struck, and if each electron striking the surface has the same chance of any particular future as if it had struck in combination with an X atom as an ion, then the ratios of the numbers leaving the surface will be independent of the existence of equilibrium in the adjacent gas phase. If this is the case, and we have quasi-equilibrium between the gas and surface phases, i.e., if the gas phase contains only cold X atoms, or even

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[1] J. Franck, Zeits. f. Physik **5**, 428 (1921).

[2] Angener and Müller, Zeits. f. Physik **26**, 643 (1925).

[3] See Max Born, *Probleme der Atomdynamik.*, Berlin, Julius Springer, p. 150 (1926).

[4] J. E. Mayer and L. Helmholz, Zeits. f. Physik **75**, 19 (1932).

[5] J. E. Mayer, Zeits. f. Physik **61**, 798 (1930).

[6] L. Helmholz and J. E. Mayer, J. Chem. Phys. **2**, 245 (1934).

only cold X_2 molecules at a temperature $T_0 < T_s$, but the total mass of X leaving the surface as molecules, atoms, or ions is equal to the total mass striking the surface, say only as X_2 molecules, then the relative numbers of ions, atoms and electrons leaving the surface still enable the calculation of the equilibrium constant in the gas phase and of the standard free energy change of reaction (1).

In the special case that the temperature is so high and the pressure so low that almost complete dissociation of X_2 into X is called for, and if $Z_{x^-} \ll Z_x$ we may write $Z_x = 2Z_{x_2}$, where Z_x gives the number of atoms leaving unit surface per unit time, and Z_{x_2} the number of molecules striking. For Z_{x_2} the relation (2) holds, and remembering that $m_{x_2} = 2m_x$ we obtain in place of (3)

$$e^{-\Delta F/RT_s} = \frac{Z_{x^-}}{Z_{e^-}} \cdot \frac{1}{P_{x_2}} \left(\frac{T_G}{2T_s} \frac{m_{x^-}}{m_{e^-}} \right)^{\frac{1}{2}} = \frac{i_{x^-}}{i_{e^-}} \cdot \frac{1}{P_{x_2}} \left(\frac{T_G \cdot m_{x^-}}{2T_s \cdot m_{e^-}} \right)^{\frac{1}{2}}. \quad (4)$$

In the last part of (4) use is made of the fact that the ratio of the numbers of electrons and ions leaving the surface is equal to the ratio of the current carried by the electrons, i_{e^-}, to that carried by the ions, i_{x^-}.

From the measurements of P_{x_2}, i_{e^-} and i_{x^-}, ΔF may be evaluated (Eq. (4)), and from this by the simple calculation indicated in Eq. (5) the electron affinity, $-\Delta E_0$.

$$\Delta F = \Delta H - T_s \Delta S = \Delta E_0 + \int_0^{T_s} \Delta C_P dT - T_s \Delta S, \quad (5)$$

where ΔH, ΔS and ΔC_p have the usual significance. Since reaction (1) involves only monatomic gases, and since the temperature T_s is always so low that the internal energy is either negligible or may be readily calculated, the evaluation of ΔS and ΔC_P is easily made.

Thus one is able to determine the electron affinity of X through observation of the current i_{e^-} and i_{x^-} carried by the electrons and ions, respectively, leaving a heated surface of known temperature T_s in an atmosphere of X_2 molecules at known pressure P_{x_2}. The currents i_{e^-} and i_{x^-} may be readily measured independently of one another by magnetic removal of the electron current.

One assumption only is made, namely that there is zero reflection coefficient at the heated surface for all atomic species.

Regarding this assumption little can be said of an absolutely conclusive nature. It is known that iodine molecules dissociate completely to atoms on a hot tungsten filament,[7] and also that caesium atoms lose electrons completely on contact with a surface of high work function.[8]

The experiments here reported cover a 130°K range of temperature and a fourteenfold range of iodine pressure, in which range the apparent work function of the tungsten filament changed by 0.4 volt and differed by almost 1 volt from the true work function of clean tungsten, probably showing varying degrees of coating of the filament. In this range the calculated electron affinity showed no trend, indicating a constant reflection coefficient; a rather remarkable circumstance if the reflection coefficients were not essentially zero. It is to be emphasized here that a 10 percent reflection coefficient would introduce an error of only RT ln 1.1 or about 0.4 kcal. in the calculated electron affinities, a 50 percent reflection coefficient, on the other hand, would introduce a very appreciable error of 2.7 kcal.

A temperature and surface independent reflection coefficient for electrons of exactly $\frac{1}{2}$ may possibly exist, as indicated by the fact that there is a twofold discrepancy in the thermionic emission constant for electrons as obtained by experiment and as calculated by modern theory.[9] The calculation of electron affinities according to Eq. (4) assumes tacitly that the theoretical electron emission equation is correct, and that the experimental discrepancy is due to some such phenomenon as a temperature dependent work function. Should subsequent investigations of the theory of electron emission indicate that there does exist a reflection coefficient of $\frac{1}{2}$ for electrons on metal surfaces (as would be obtained if image forces were neglected in the

[7] Personal communication from I. Langmuir.
[8] Langmuir and Kingdon, Proc. Roy. Soc. **A107**, 61 (1925). Kingdon, Phys. Rev. **21**, 510 (1924).
[9] See for example S. Dushman, Rev. Mod. Phys. **2**, 381 (1930).

original calculation), then the values of electron affinities reported in this paper should all be raised by about 2.7 kcal.

Apparatus

The apparatus finally evolved for the purpose of measuring ion and electron currents under the conditions outlined above consists in the electron tube shown in simplified form in Fig. 1 and described below.

A vertically suspended filament, F, which can be electrically heated and whose temperature, T_s, may be accurately determined, is closely surrounded by a cylindrical grid, G, concentric with it; G being in turn surrounded by the concentric plate P of such size that the radius of G is approximately one-third that of P. The whole tube is surrounded on the outside by the solenoid S concentric with F. By a suitable electrical system G and P may be maintained at the potentials V_G and V_P, respectively, with $V_P > V_G > 0$ and with $V_F = 0$; by means of the galvanometer, E, connected in series with F, current flow to the plate may be detected.

If now this tube is filled with X_2 vapor at a definite pressure and the filament temperature raised to a determined value, equilibrium (1) will exist on the surface of the latter and, according to the previous considerations, X^- ions and electrons will be emitted. Both ions and electrons travel radially in straight lines to the plate where they are collected and recorded as a galvanometer deflection, Δ_e-, moreover since Z_X-$\ll Z_e$- this deflection may be considered as due to only the electrons and hence i_e- is simply calculated from Δ_e-.

If now a current is passed through the solenoid the tube operates as the familiar magnetron set-up and the electron current is prevented from reaching the plate P. In high vacuum ($<10^{-6}$ mm) the electron current to P may be completely (to less than the 10^{-6} part of its original value) eliminated by solenoid currents about 4 times greater than that theoretically necessary to deflect the electron beam into a circle of diameter equal to the radius of the plate P. In the presence of an inert gas (Hg vapor at 2×10^{-3} mm) a slightly higher solenoid current (5 or 6 times the theoretical) is necessary to eliminate the electron current to P. These solenoid currents, however, have no appreciable effect on the current due to the heavy ions, and thus ion currents i_X- as well as the electron current i_e- may be independently determined under fixed conditions of P_{x_2} and T_s.

Details of construction of the electron tube used in the measurements on iodine together with its electrical circuit are shown in Fig. 2.

The tube itself consists of two parts, the body, A, which also acts as a plate support, of Pyrex glass shaped as shown and the grid-filament support and leads sealed in the Pyrex cap, C. This cap fits on A and is united with it by sealing, thus affording a vacuum-tight joint free from grease which is easily opened for repairs. In addition, A is fitted with an exhaust tube, Q, by means of which evacuation is accomplished.

The collecting plate B (4.75 cm diam., 6.75 cm long) fits snugly into supports in A and

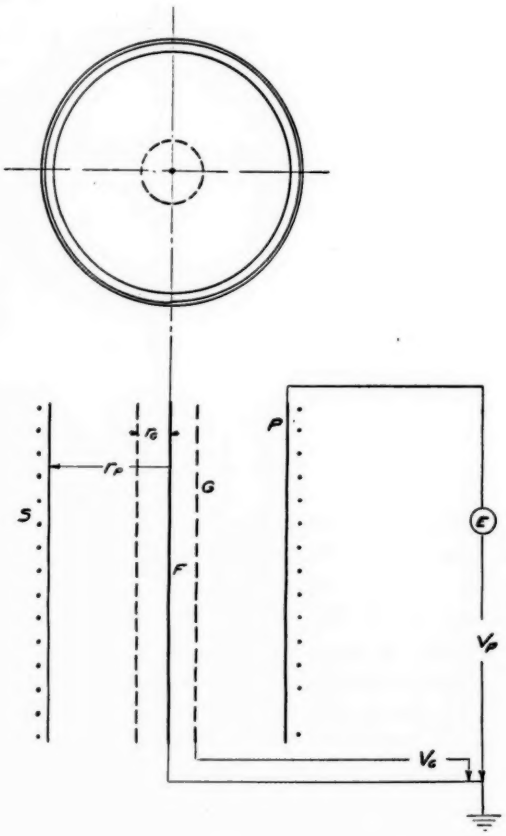

Fig. 1.

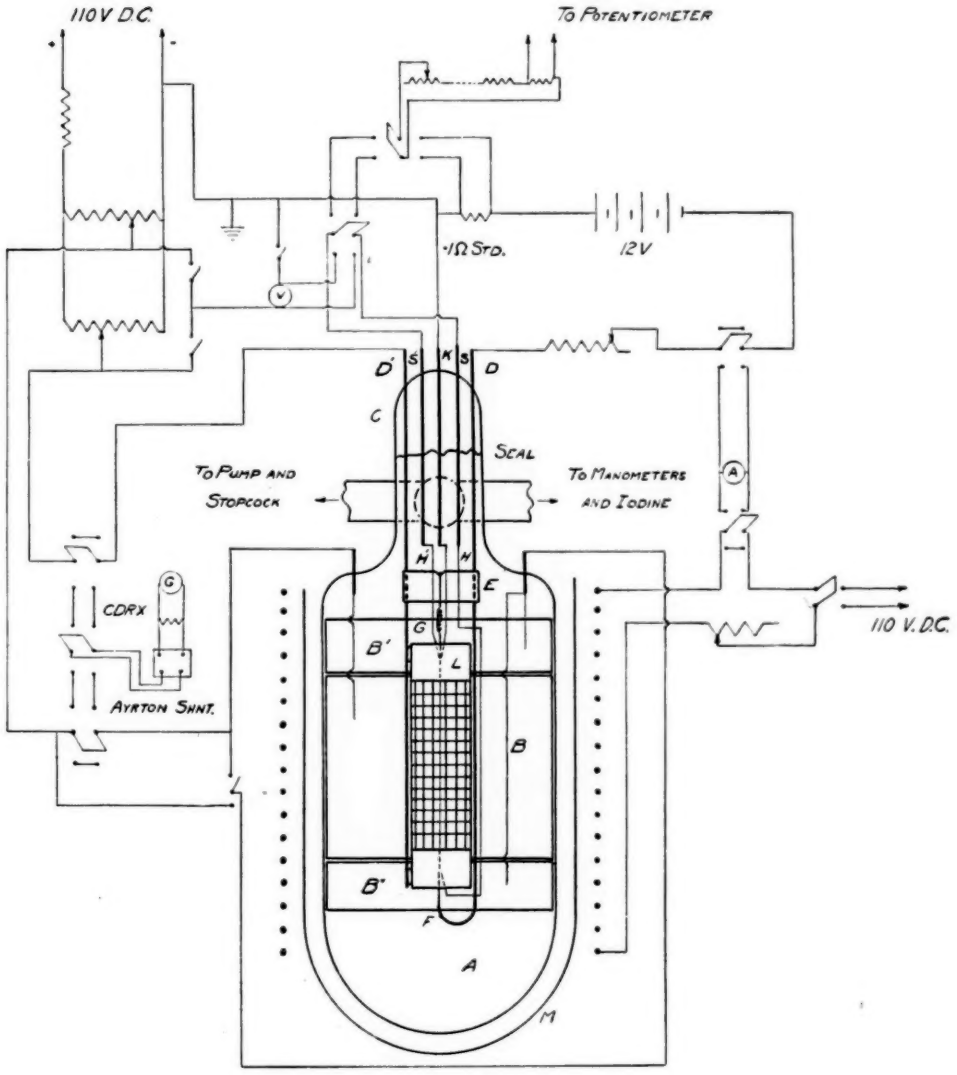

FIG. 2.

between the guard plates B' and B'' at a distance of 1.5 mm from each. These plates are of Monel sheet bent into cylindrical form and welded; electrical contact is made with them by tungsten wires sealed through the tube shoulders. (B is in the galvanometer circuit during all measurements of plate current, B' and B'' are connected in series, charged to the same potential as B but not in the galvanometer circuit, their purpose being to prevent the registering of stray currents and to insure uniformity of the electrical field.)

The grid-filament holder is built up around the two tungsten rods D, D' (2.1 mm diam.) sealed in the cap C as sketched, the rods serving in addition as electrical leads. For support D and D' are fused in the glass block E, and D' has welded at its lower end the Monel filament clamp F.

The filament of General Electric pure tungsten wire (8.77 cm long, 0.019 cm diam.) is supported as indicated by the helical tungsten spring, G, hung from F, serving to keep it taut and in position even at white heat. A flexible nickel wire welded to K constitutes the second filament lead. Exactly at the extreme ends of the filament are welded two fine nickel wires H and H' which

connect to the short tungsten rods S and S' and enable the potential drop across the filament itself to be accurately measured.

The grid L (6.28 cm long, 1.25 cm diam.) welded to D is of Monel gauze (25 mesh) and is fitted at either end with solid rings M and M' (1.61 cm long). Such an arrangement allows charged particles from only the central portion of the filament to reach the plate through the grid, thus assuring that all of the latter registered as a plate current shall have come from a region of uniform temperature. Both grid and filament are so adjusted as to hang in the center of the tube.

Finally all exposed parts of the rods D, D', S, S' and K are sealed in Pyrex to cut down gas evolution on heating.

The body of the tube is surrounded by the cylindrical Pyrex jacket, M, through which cooling water can be continually passed. This cooling eliminates plate heating through filament radiation and serves the double purpose of retarding gas evolution and preventing electrical leakage.

Through Q connection is made to a simple high vacuum line activated by a two stage Pyrex mercury diffusion pump with the necessary backing and containing a carefully calibrated McLeod gauge accurate in the range from 1.0×10^{-5} to 5×10^{-3} mm. To protect the tube from back diffusion of mercury vapor and stopcock grease (Apiezion "L" was used) several liquid air traps of the usual variety were placed in the line at strategic points, the last of these being separated from the tube by the greaseless stopcock as illustrated in Fig. 2A. This was of the type that contains a small glass encased iron bar and is operated magnetically and had been particularly well ground; it would hold, against a flat vacuum, pressures of 10^{-3} mm for thirty minutes without noticeable leakage. Thus one was enabled by closing this valve to build up pressure of condensable gases to this order of magnitude in the tube independently of the trap temperatures. In order that the pressure in the tube under these conditions might be measured connection is also made through Q with two quartz fiber manometers. One of these was of the ordinary bent loop style, the other being in the form of a bent loop with a small hollow Pyrex ball sealed at the apex. The ball served to increase the period of the fiber, but made reading the manometer much more rapid and trustworthy and satisfactory at higher pressures. Both manometers were calibrated with a great deal of care against the McLeod gauge in various pressures of air, the fact that the calibration curves were accurately linear indicating the latter to be essentially correct. In order to be doubly certain on this point a pressure of mercury vapor was allowed to build up in the system through the warming of the liquid air traps. From the temperature of the system this pressure could be accurately calculated and using the manometer calibration curve it could be determined experimentally; the two values agreed to within 0.1 micron. In practice it was found that measures of the same pressure carried out on the two manometers never differed by as much as 10.0 percent.

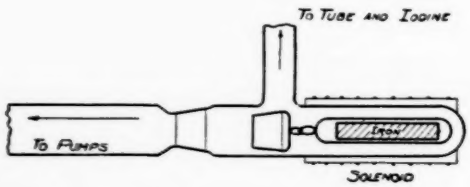

FIG. 2A. Magnetic stopcock.

The iodine used in this investigation was prepared in ampules as described below and stored in an ampule holder sealed to Q. Iodine as needed was admitted to the evacuated system through breakage of the individual containers by a small magnetic hammer and was distilled into and retained in a special trap in the line.

Thus concluding the description of the vacuum system, there remain only a few remarks to be made regarding the electrical circuit. In order to determine precisely the temperature of the filament from its volt-ampere characteristics it was necessary to measure accurately the potential drop across the filament and the current flowing through it. The first of these was carried out directly with the potentiometric set-up indicated, the second indirectly as the potential drop across a standard 0.1 ohm resistance. In this manner observations could be obtained accurate

to 1.5 percent (an accuracy of 10°K in the measurement of T_s), the high resistances in the potentiometer circuit insuring that the current flow through the latter be less than 0.01 of the total.

The solenoid consisted of three windings of enameled copper wire (B.S. gauge No. 24) or fifty-four turns per centimeter on an insulated brass tube and was 7.6 cm in diameter and 24.2 cm long. It was, in addition, water-cooled to prevent variations in the field strength due to temperature increase of resistance. The magnetic field produced by it in the electron tube was not uniform for two reasons: first no account was taken in regard to proper orientation in the earth's magnetic field and second there was an inhomogeneity produced due to the end effect—the deviations from uniformity are small, however, and for our purpose are not important.

The galvanometer used was a Leeds and Northrup HS type having as set up a sensitivity of 5.72×10^{-11} amp./mm; equipped with the Ayrton shunt shown, currents as high as 1.0×10^{-3} amp. could be measured on it. Finally the whole electrical circuit was carefully insulated by sealing on wax blocks so that under running conditions any electrical leak which may have existed was undetectable as a galvanometer scale deflection.

Measurements

Both the iodine used and the vacuum line were specially treated. The former was Baker's best C.P. reagent grade and was subject to a triple fractional distillation in a well baked vacuum system under constant pumping with a view to removing chemical impurities such as chlorine and bromine and to the elimination of occluded gases. The accomplishment of this last appeared very difficult since even after long pumping there was still a slight residue of non-condensable gases evolved on vaporizing the iodine; past a certain point pumping seemed to have no affect toward remedying this condition. Since, however, this evolution was never responsible for a pressure in the system of greater than $1.0\text{–}2.0\times10^{-4}$ mm it was practically negligible for the purpose at hand. The iodine after distillation was collected and sealed off in vacuum in special thin bottomed ampules, these latter being placed in the holder previously mentioned.

After assembly electron tube, vacuum line and manometers were baked with electric furnace and hand torch at 400°C for three hours in a vacuum of 10^{-4} mm or better. At the end of this time the electron tube was heated to glowing with an induction furnace and torching of the line repeated. Finally the filament was heated, the temperature gradually raised to 2600°K and held there for two hours keeping the pressure $<10^{-5}$ mm and a final heating with torch and induction furnace carried out. After completing this process the pressure would in twenty-four hours rise from $<10^{-6}$ mm to $<10^{-5}$ mm with the pump shut off or it would rise a like amount in thirty minutes with the pump shut off and the filament at 2200°K. Such conditions were satisfactory for the present purpose since these pressures of residual gases were responsible for a quantity of negative ions too small to be experimentally detected.

Before each run the filament was aged as recommended by Langmuir and Jones[10] by heating in the water-cooled tube to 2600°K for an hour with continued pumping. After this time the temperature was lowered to running value and held there until the electron emission, as calculated from the observed plate current, had reached a constant value which was approximately equal to the theoretical. The system was then in condition for measurements.

The measurements made consisted in the observation of the plate current as a function of the solenoid current under various conditions of filament temperature and gas pressure. In each set of measurements the temperature of the exposed section of filament was determined from the filament voltage and current by means of the tables of Langmuir and Jones,[10] correction being made for the cooling effect of the leads. The grid and plate potentials were adjusted on the voltmeter and pressures read on either the McLeod gauge or the fiber manometers.

The first two sets of observations were in the nature of controls and were carried out in

[10] Langmuir and Jones, Gen. Elec. Rev. **419**, 310 (1927); Table I, function No. 6.

vacuum and in mercury vapor, respectively, the purpose of the first being to determine the efficiency of the solenoid in cutting out the electron current and that of the second to determine the extent of decrease of this efficiency caused by scattering during collisions of electrons and heavy atoms of negligible electron affinity. From the nature of these measurements the conditions under which they were performed (see Table I) were purposely so chosen as to be very unfavorable to electron current extinction compared with those later used for iodine. The first set was conducted in a good vacuum (10^{-6} mm or better) with the pumps running and mercury vapor frozen out; the second set in an atmosphere of mercury (1.84×10^{-3} mm pressure) built up by warming the traps to room temperature.

At the end of these two runs the same determinations were carried out in known pressures of iodine vapor at various filament temperatures. The system was freed from mercury vapor by freezing the line traps with liquid air, the pumps shut off by a mercury seal, the magnetic valve closed and iodine admitted by breaking one of the ampules. The iodine was distilled into the small trap previously mentioned, the temperature of which was maintained at some fixed value in the range from -40°C to -10°C by a cooling alcohol bath contained in a stoppered Dewar. The value of the iodine pressure, which was determined by the bath temperature, was measured on the manometers with the filament at running temperature and the tube walls water-cooled. (Further discussion regarding the pressure measurements is given below.) When the pressure, as measured, had reached a constant value observations of the plate current were carried out. On their completion the iodine was frozen out of the tube by cooling the source with liquid air, the magnetic valve opened and the pressure of non-condensable gases read on the McLeod gauge. This procedure was repeated for various iodine pressures and filament temperatures, with intervals of pumping.

Calculations and Results

Combining Eqs. (4) and (5) and solving for $-\Delta E_0$, the electron affinity, one obtains

$$-\Delta E_0 = RT_s \ln\left[\frac{i_{x^-}}{i_{e^-}}\frac{1}{P_{x_2}}\left(\frac{T_G m_{x^-}}{T_s 2m_{e^-}}\right)^{\frac{3}{2}}\right] + \int_0^{T_s}\Delta C_P dT - T_s\Delta S. \quad (6)$$

For bromine the difference between the atomic ground level, a $^2P_{3/2}$ level, and the next level $^2P_{1/2}$ is 0.45 volt. The value of $e^{-\epsilon/RT}$ at 2000°K is seen to be 0.074, and hence one may neglect the contribution to either specific heat or entropy due to internal excitation. For iodine the energy difference between these two levels is greater. The ions presumably have no excited state lower than 1 volt. The lowest level for all the halogen atoms, a $^2P_{3/2}$ level, has a weight 4, that for the ions, a $^1S_0$ level, a weight 1, whereas the electron has a weight 2.

One may then write for the reaction 1, under consideration, that

$$\int_0^{T_s}\Delta C_P dT = (5/2)RT_s$$

the difference in entropy between atom X and ion X^- is R ln 4, and the entropy of the electron gas, at hypothetical 1 atmosphere pressure, is given by the Stern-Tetrode expression

$$S_{e^-} = R \ln\left[k(2\pi m_{e^-} kT_s)^{3/2}h^{-2}\cdot 2T_s e^{5/2}\right].$$

Making the numerical evaluations and introducing logarithms to the base 10 one obtains for $-\Delta E_0$

$$-\Delta E_0 = (4.575/1000)T_s[\log \Delta_{I^-}/\Delta_{e^-} - \log P_{I_2} + 2\log T_s + 4.073]\text{kcal. for } I. \quad (7)$$

Besides P_{x_2} and T_s the ratio of the galvanometer deflections $\Delta_{I^-}/\Delta_{e^-}$ due to ion and electron current only enters this equation.

In Fig. 3 is shown a typical example of how the electron current to the plate falls off with increasing solenoid current. The plate current, expressed as the fraction of that existing in the absence of the magnetic field, is plotted on a logarithmic scale against the reciprocal of the solenoid current. The curve marked vacuum is for residual gas pressures lower than 10^{-6} mm Hg, the curve marked Hg was observed with 1.8×10^{-3} mm of mercury vapor present in the

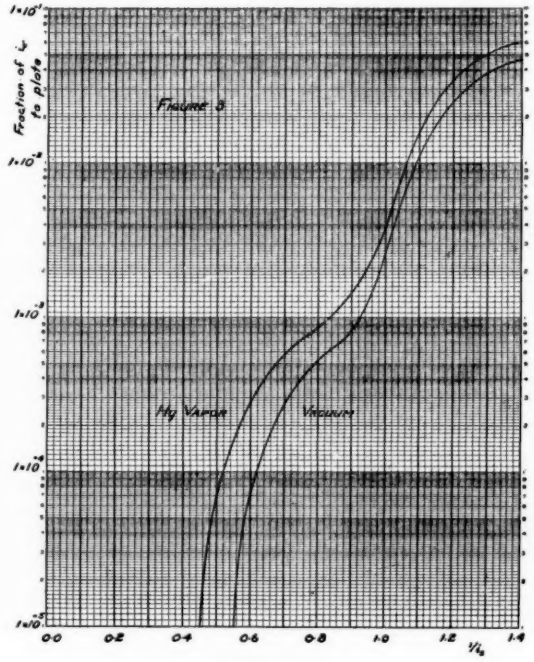

FIG. 3.

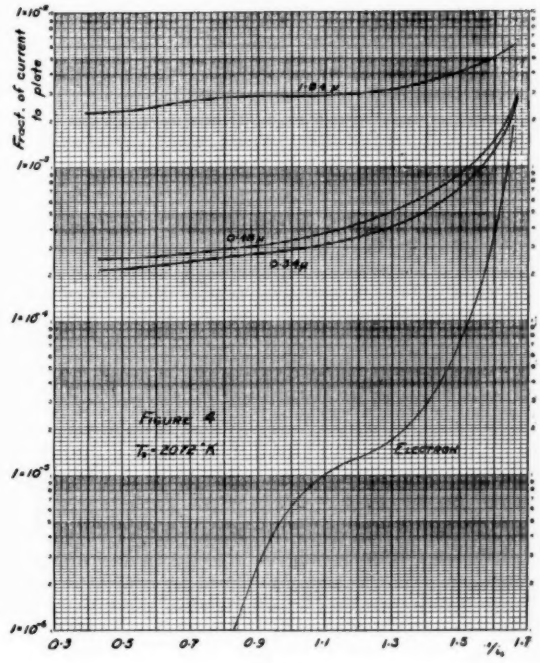

FIG. 4.

tube. The grid potential (compared to filament zero), was 20.0 volts, and the plate potential 30.0 volts. The filament temperature was 2100°K. Even under these comparatively unfavorable conditions of high potentials, high filament temperatures, and high residual gas (Hg) pressure the electron current could be eliminated satisfactorily.

Fig. 4 shows the same type of plot for a set of typical experiments with iodine. In this case the grid and plate potentials were 9.0 and 10.0 volts, respectively, and the filament temperature 2072°K. The curve marked "electron" shows the behavior of the plate current under these conditions in the absence of iodine vapor; the three other curves were obtained with 0.34, 0.48 and 1.84 microns (1 micron $=10^{-3}$ mm Hg) of iodine vapor pressure, respectively. Extrapolation to $1/i_s=0$ (infinite solenoid current), which can be readily made, gives, directly the desired ratio, Δ_I-/Δ_e- to an apparent accuracy of within 20 percent.

The filament temperatures used were about 2000°K and the factor $4.575T/1000$ in Eq. (7) has the numerical value 9.2 kcal. at this temperature. An error of 20 percent in Δ_I-/Δ_e- introduces an error of about 0.7 kcal. in the final result, as would a 20 percent error in the measurement of P_{x_2}. Errors in the measurement of T_s, the filament temperature enter in such a way that a 20° or 1 percent error in the temperature introduces a 1 percent or 0.7 kcal. error in the electron affinity. It would appear that the errors introduced from these three causes could not exceed 2 kcal. and most probably are considerably less, since there is no apparent reason why the pressure measurements should not have been good to 10 percent and the temperatures to within $\frac{1}{2}$ percent.

The pressure of iodine in the apparatus, as measured by the quartz fiber manometers, did not, until a considerable time had elapsed, build up to the saturation value corresponding to the temperature of the cooling bath. This interval was sometimes almost an hour after placing the bath on the previously liquid-air cooled iodine. Furthermore, on heating the filament a considerable and permanent drop in pressure due, presumably, to "clean up" effects was observed. For these reasons considerable care was taken in order to be certain that the measured pressures represented accurately the pressure existing in

the tube. As before mentioned, two quartz fiber manometers connecting directly to the tube were used; the discrepancy between the readings of the two never exceeded 10 percent.

Finally it must be emphasized that, in what seems to us the unlikely case, that the fundamental assumption of nearly zero reflection coefficient for all atom species be in error, an indeterminate error may be introduced in the values of the electron affinity presented, and particularly if there actually be a reflection coefficient of $\frac{1}{2}$ for electrons the results here published must be raised by 2.7 kcal.

TABLE I.

No.	T (°K)	P ($\times 10^3$)	Δ_I^- (cm)	Δ_e^- (cm)	Δ_I^-/Δ_e^- ($\times 10^4$)	$-\Delta E_0$ (kcal.)
1	1942	1.80	2.05	245	83.6	73.9
2	1949	1.55	1.93	243	79.3	74.5
3	1971	0.25	0.87	2050	4.24	71.1
4	2072	0.13	5.87	55300	1.07	72.2
5	2072	0.34	2.65	12500	2.12	71.1
6	2072	0.48	2.15	8300	2.61	70.5
7	2072	1.84	17.30	8550	20.3	73.4
					Ave.	72.4

In Table I the data and calculated electron affinities of the various experiments on iodine are presented.

The method of calculation here employed differs from that previously used in the similar case in which the ionization of caesium atoms to positive Cs^+ ions is observed. The essential difference is that here the work function of the metal does not occur explicitly in the calculation, but instead, the electron emission under the conditions of the experiment is directly observed. No additional assumption is involved in this method of calculation, indeed the difficulty that the work function of the metal is actually changed by the presence of the iodine atmosphere is eliminated.

It may be of interest to tabulate the difference in electron emission observed during the course of these experiments, as compared to that observed[10] from a clean tungsten surface. To present this one may choose to tabulate the value of the work function φ_{WI} of the iodine coated tungsten filament in the various experiments evaluated under the assumption that the temperature independent constant of the emission equation for such surfaces is the same as that for clean tungsten. That is, the observed electron emission in the various experiments differed from the observed emission of clean tungsten by the factor $\exp(\varphi_W - \varphi_{WI})/kT_s$ where φ_W, the work function of tungsten, is 4.48 volts and k is expressed in volts. Table II presents these values.

TABLE II. *Work function of tungsten* (φ_W) = *4.48 volts.*

T_s (°K)	1942	1949	1971	2072	2072	2072	2072
P_{I_2} ($\times 10^3$)	1.80	1.55	0.25	0.13	0.34	0.48	1.84
φ_{WI} (volts)	5.45	5.46	5.27	5.06	5.33	5.40	5.40

Although no great significance attaches to these values, and it is even conceivable that the whole effect is due to the presence of small oxygen traces, still the results are qualitatively as expected. The work function increases with increasing iodine pressure and attains a constant value at pressures of the order of magnitude of 1 micron.

The final results indicate that the electron affinity of iodine is 72.4 kcal. with a probable error of ± 1.5 kcal.

The authors wish to express their indebtedness to Mr. Harry John, glassblower of the laboratory, for his assistance and advice in the construction of the apparatus.

Families of Thermodynamic Equations. I

The Method of Transformations by the Characteristic Group

F. O. KOENIG, *Stanford University, California*

(Received November 1, 1934)

Attention is called to the fact that certain important equations of thermodynamics such as the two Gibbs-Helmholtz equations may be grouped into families, but that a precise definition of such families has hitherto been lacking. For the case of a single phase of k components in equilibrium a method is given for splitting a certain class of equations, the "f_1^1-equations," into families in a precise manner as follows. The f_1^1-class of equations is defined by means of four "basic" equations and two "basic" assumptions, and involves the $2k+8$ variables E, H, F, A, V, S, P, T, μ_i, n_i. For the f_1^1-equations there is in turn defined a number of "standard forms" which depend upon the introduction of absolute value signs in a certain way. Then the "characteristic group," a substitution group of the eighth order on the letters E, H, F, A, V, $-S$, $-P$, T, μ_i, n_i is generated by a series of geometrical operations on a square. The theorem is stated that the transformation of any f_1^1-equation in standard form by any element of the characteristic group yields an f_1^1-equation in standard form. No formal proof of this theorem is given, but its correctness is sufficiently demonstrated by systematic verification. The theorem leads immediately to the definition of a family of f_1^1-equations as the totality of distinct f_1^1-equations resulting from the transformation of a given f_1^1-equation in standard form by all the elements of the characteristic group. It is found that every f_1^1-equation is a member of one and only one f_1^1-family. The method increases the number of fundamental equations readily available and emphasizes the symmetry of these equations.

A. INTRODUCTION

1. The existence of families of thermodynamic equations

It has been recognized since the work of Gibbs that many of the important equations of thermodynamics fall into families of marked algebraical symmetry. Of this the Gibbs-Helmholtz equations are a well known example:

$$E=A-T(\partial A/\partial T)_{V,\ n_i}, \tag{1.1}$$

$$H=F-T(\partial F/\partial T)_{P,\ n_i}.^{1} \tag{1.2}$$

Hitherto the recognition of these families seems to have been more intuitive than explicit, in that it has to the author's knowledge never been exactly stated what constitutes such a family. Thus no immediate answer suggests itself to the question whether the family to which Eqs. (1.1) and (1.2) belong has any further members, and, if so, how the latter may be found.

2. Method of the present paper

This paper (communication I) gives a method for splitting an important class (defined below and referred to as the "f_1^1-class") of thermodynamic equations into families. The method consists in deducing the family to which a particular equation of the class in question belongs, by writing the equation in a certain form (the "standard form") and then transforming it by the elements of a certain substitution group (the "characteristic group"). This group in turn can be generated geometrically.

3. The thermodynamic system to be considered

The definitions of the class of equations in question and of the corresponding substitution group depend somewhat upon the type of thermodynamic system considered. In this paper only one type of system will be dealt with, namely an open system made up of an arbitrary number $k(k\geq 1)$ of components in a single phase (volume phase) in internal equilibrium. An open system is one in which the amounts of the components and consequently the total mass are freely variable. For simplicity it is assumed that the pressure is the same at each point within the phase, i.e., that gravity is absent. External electric and magnetic fields are also assumed to be absent or of negligible influence.

The treatment of certain other types of systems will be given in a later paper.

[1] The meaning of all symbols is given below.

B. The Fundamental Thermodynamic Equations (f_1^1- and f_2^1-Equations) of the System

1. Necessity of defining the f^1-class of equations

The class of thermodynamic equations which can be resolved into families by the group method developed in this paper is part of a larger class of equations which are properly regarded as the fundamental thermodynamic equations of the system and which for reasons apparent in a later paper (communication II) will be referred to as the "fundamental equations of the first order of generality" or abbreviated, as the f^1-equations. It is expedient to define first the larger class of the f^1-equations and then the subclass which can be treated by the group method in question.

2. The basic equations

The definition of the f^1-class of equations depends upon four equations which will be known as the basic equations. These are conveniently taken to be:

$$E=H-VP, \tag{2.1}$$

$$H=F+ST, \tag{2.2}$$

$$F=A+PV, \tag{2.3}$$

$$dE=-PdV+TdS+\sum_i \mu_i dn_i. \tag{3}$$

E, H, F and A denote, respectively, the energy, heat content, Gibbs free energy and Helmholtz free energy of the system, and are called the characteristic functions. V, S, P, T, μ_i and n_i denote, respectively, the volume, entropy, pressure, temperature, chemical potential of the ith component and amount of the ith component.

3. The basic assumptions

In addition to the basic equations there are necessary for the definition of the f^1-equations two physically valid assumptions, to be known as the basic assumptions. They are the following: (i) The $k+3$ differentials appearing in Eqs. (3) are total differentials. (ii) E is a homogeneous function of the first order in the $k+2$ capacity factors V, S, n_i.

4. The f^1-equations

Such equations in any or all of the $2k+8$ variables E, H, F, A, V, S, P, T, μ_i, n_i as can by mathematical operations be obtained from the four basic equations and no physical assumptions other than the two basic assumptions will be known as the f^1-equations. The four basic equations are evidently members of the class of f^1-equations because any equation can be obtained from itself, e.g., through multiplication by unity. It is furthermore evident that the particular Eqs. (2), (3) do not represent the only possible choice of basic equations: any set of three equations defining three of the characteristic functions in terms of the fourth and of V, S, P, T will serve as well as the particular set (2), and Eq. (3) may be replaced by any one of the other three general Gibbsian equations (see Eqs. (13) below) of the system.

5. Division of the f^1-class into the f_1^1- and the f_2^1-classes

The thermodynamic equations subject to the group method described in this paper form a subclass of the f^1-class comprising only such f^1-equations as do not depend upon basic assumption (ii) above. This subclass will be known as the "f^1-equations of the first kind," or abbreviated, as the f_1^1-equations. The basic Eqs. (2), (3) and the Gibbs-Helmholtz Eqs. (1) are examples of f_1^1-equations.

Such f^1-equations on the other hand as depend upon basic assumption (ii) will be known as the "f^1-equations of the second kind," or f_2^1-equations. An example is the equation:

$$E=-PV+TS+\sum_i \mu_i n_i \tag{4}$$

obtained by applying Euler's theorem to (3). The f_2^1-class cannot be split into families by the group method of this paper. A method less elegant but powerful enough to resolve the entire f^1-class will be given in a later paper (communication II).

C. The f_1^1-Equations in Standard Form

The method described below (Parts E and F) necessitates writing the f_1^1-equations in certain forms to be known as "standard." These stand-

ard forms yield no new information: they are merely a mathematical device. For any given f_1^1-equation the standard forms are defined by the following two rules: (i) If the equation contains both P and V then *either* the letter P wherever it occurs *or* the letter V wherever it occurs is to be enclosed in an absolute value sign, thus: $|P|$ or $|V|$. Which of the two letters is so enclosed is immaterial. If the equation contains only P without V, or *vice versa*, the letter present is to be left unchanged. (ii) A procedure similar to (i) is to be applied to the letters T and S. Eq. (2.1) for example has two standard forms:

$$E=H-|V|P, \quad E=H-V|P|. \quad (5.1), (5.2)$$

It is clear that as regards standard forms there are only three types of f_1^1-equations, characterized by one, two and four standard forms and illustrated by Eqs. (1), (2) and (3), respectively.

If any given f_1^1-equation is written in any one of its standard forms, the resulting f_1^1-equation will be said to be "in standard form," and if every equation of the f_1^1-class is imagined to be written in every one of its standard forms, the result will be referred to as the "f_1^1-class in standard form."

Since for any system in thermodynamic equilibrium (Part *A*) the quantities P, V, T, S are essentially positive, writing the f_1^1-equations in standard form incurs no loss of generality.

D. The Characteristic Group and the Characteristic Array

1. The characteristic group

The central part in the resolution of the f_1^1-class into families is played by a set of eight substitutions on the ten letters E, H, F, A, V, $-S$, $-P$, T, μ_i, n_i. This set of substitutions moreover forms a group because it can be obtained by a geometrical method of a type often used to generate groups.

Fig. 1a represents a square of which each side is regarded as belonging to one of the four characteristic functions E, H, F, A in the definite order shown, and each vertex to one of the four variables V, $-S$, $-P$, T also in the definite order shown. It may be noted that corresponding intensity and capacity factors occupy opposite

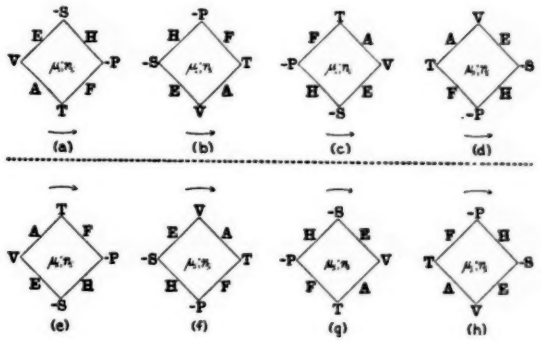

FIG. 1.

vertices and have opposite signs. The center of the square belongs to the k pairs of variables μ_i, n_i. By rotation and reflection of Fig. 1a in its plane the seven Figs. 1b, $\cdots$ 1h can be generated. The superposition of any two figures brings about a superposition of letters which is definite except for μ_i and n_i. This indefiniteness is removed by the convention that μ_i and n_i always fall upon themselves. Superposition of any particular pair of figures then becomes symbolic of the substitution of the set E, H, F, A, V, $-S$, $-P$, T, μ_i, n_i by a particular one of its permutations. It is readily verified that the superposition of Figs. 1a, $\cdots$ 1h upon themselves and upon one another in all possible pairs leads to a group of but eight distinct substitutions, s_1, $\cdots$ s_8, as follows:

$$s_1=\begin{pmatrix} E & H & F & A & V & -S & -P & T & \mu_i & n_i \\ E & H & F & A & V & -S & -P & T & \mu_i & n_i \end{pmatrix},$$

$$s_2=\begin{pmatrix} E & H & F & A & V & -S & -P & T & \mu_i & n_i \\ H & F & A & E & -S & -P & T & V & \mu_i & n_i \end{pmatrix},$$

$$s_3=\begin{pmatrix} E & H & F & A & V & -S & -P & T & \mu_i & n_i \\ F & A & E & H & -P & T & V & -S & \mu_i & n_i \end{pmatrix},$$

$$s_4=\begin{pmatrix} E & H & F & A & V & -S & -P & T & \mu_i & n_i \\ A & E & H & F & T & V & -S & -P & \mu_i & n_i \end{pmatrix},$$

$$s_5=\begin{pmatrix} E & H & F & A & V & -S & -P & T & \mu_i & n_i \\ A & F & H & E & V & T & -P & -S & \mu_i & n_i \end{pmatrix}, \quad (6)$$

$$s_6=\begin{pmatrix} E & H & F & A & V & -S & -P & T & \mu_i & n_i \\ E & A & F & H & -S & V & T & -P & \mu_i & n_i \end{pmatrix}$$

$$s_7=\begin{pmatrix} E\ H\ F\ A & V\ -S\ -P & T\ \mu_i\ n_i \\ H\ E\ A\ F & -P\ -S\ V & T\ \mu_i\ n_i \end{pmatrix},$$

$$s_8=\begin{pmatrix} E\ H\ F\ A & V\ -S\ -P & T\ \mu_i\ n_i \\ F\ H\ E\ A & T\ -P\ -S & V\ \mu_i\ n_i \end{pmatrix}.$$

In the condensed notation used in the theory of groups the substitutions (6) become:

$$\begin{aligned} s_1&=I, \\ s_2&=(E\ H\ F\ A)(V\ -S\ -P\ T), \\ s_3&=(E\ F)(H\ A)(V\ -P)(-S\ T), \\ s_4&=(E\ A\ F\ H)(V\ T\ -P\ -S), \\ s_5&=(E\ A)(H\ F)(-S\ T), \\ s_6&=(H\ A)(V\ -S)(-P\ T), \\ s_7&=(E\ H)(F\ A)(V\ -P), \\ s_8&=(E\ F)(V\ T)(-S\ -P). \end{aligned} \qquad (7)$$

That these substitutions form a group is readily confirmed by constructing their multiplication table, here omitted for brevity.

Each individual substitution, or element, of the group (6) [or (7)] may be regarded as the product of a substitution on E, H, F, A by one on $V, -S, -P, T, \mu_i, n_i$.[2] Because the group thus correlates certain substitutions on the characteristic functions with certain substitutions on the variables $V, -S, -P, T, \mu_i, n_i$ it will be called the "characteristic group."

2. The characteristic array

In what follows it will often be necessary to introduce the substitutions of the characteristic group into a given equation (always an f_1^1-equation in standard form), an operation known as transforming the equation by the elements of the group. For this purpose the following summary of the substitutions (6) in the form of an array of eight rows and ten columns is useful:

$$\begin{array}{l|lll|l|l} E\ H\ F\ A & V & -S & -P & T & \mu_i\ n_i \\ H\ F\ A\ E & -S & -P & T & V & \mu_i\ n_i \\ F\ A\ E\ H & -P & T & V & -S & \mu_i\ n_i \\ A\ E\ H\ F & T & V & -S & -P & \mu_i\ n_i \\ \hline A\ F\ H\ E & V & T & -P & -S & \mu_i\ n_i \\ E\ A\ F\ H & -S & V & T & -P & \mu_i\ n_i \\ H\ E\ A\ F & -P & -S & V & T & \mu_i\ n_i \\ F\ H\ E\ A & T & -P & -S & V & \mu_i\ n_i \end{array} \qquad (8)$$

Inspection of the four square areas marked off by the dotted lines shows plainly how the substitutions of the characteristic group are interrelated through cyclic permutation. The array (8) may be regarded as derived from its first row by superposing the eight Figs. 1, in the order 1a, ··· 1h, upon Fig. 1a. Because it is closely related to the characteristic group, the array (8) will be known as the "characteristic array."

The characteristic array is of interest not merely for the above-mentioned practical reason, but also because it can be used to resolve the f_2^1-class of equations, which does not yield to the group method here described, into families; this will be shown in a later paper.

E. The Method for the Deduction of Families of f_1^1-Equations

1. Relation of the f_1^1-class to the characteristic group

The property which leads to the definition of families of f_1^1-equations is expressed by the following theorem: *The transformation of any f_1^1-equation in standard form by any element of the characteristic group yields an f_1^1-equation in standard form.* A more compact statement is the following: *The f_1^1-class in standard form is invariant under the characteristic group.* The rigorous proof of these theorems transcends the scope of this paper. Their correctness may be regarded as established by the examples given below (Part F).

2. Definition of the f_1^1-families

The first of the above statements leads directly to the following definition: The totality of distinct f_1^1-equations resulting from the trans-

[2] The latter substitution is formally identical with one on $V, -S, -P, T$ alone because μ_i and n_i always replace themselves. The group (6) [or (7)] thus defines two sets of substitutions on four letters each. The members of these sets are formally similar and moreover each set alone forms a group of the eighth order, the so-called octic group. From the formal point of view the group (7) is thus one of the simple isomorphisms between the two octic groups on the letters E, H, F, A and $V, -S, -P, T$, respectively.

formation of a given f_1^1-equation in standard form by all the elements of the characteristic group will be called a family of f_1^1-equations or an f_1^1-family.

This definition may be supplemented by two others: (i) The individual distinct f_1^1-equations constituting an f_1^1-family will be known as its members. (ii) Two f_1^1-equations will be regarded as distinct if they cannot be converted into each other by operations which besides the two f_1^1-equations themselves involve only algebraic identities, and they will be regarded as identical if they can be so converted. Definition (ii) regards as identical any two f_1^1-equations the differences between which are "trivial," because the operations by which such differences can be removed, e.g., transposition, rearrangement of terms in accordance with the formal laws of algebra, introduction or removal of absolute value signs, simple changes of algebraic sign, cancellation of terms by subtraction or division, etc., can be looked upon as derived from algebraic identities.

3. Theorems on f_1^1-families

It is readily verified that: (i) The f_1^1-families arising from a given f_1^1-equation in its various standard forms are all identical, i.e., from a given f_1^1-equation one and only one f_1^1-family can arise. (ii) The f_1^1-families arising from all the members of a given f_1^1-family are all identical, i.e., every f_1^1-family is invariant under the characteristic group. It follows that: (iii) Every f_1^1-equation is a member of one and only one f_1^1-family.

4. Consideration of a particular case

The above principles may be illustrated by examining in some detail the deduction of the family corresponding to the f_1^1-equation:

$$(\partial T/\partial V)_{S,\,n_i} = -(\partial P/\partial S)_{V,\,n_i}. \qquad (9)$$

This equation evidently has four standard forms. If the particular form chosen is:

$$(\partial |T|/\partial V)_{S,\,n_i} = -(\partial |P|/\partial S)_{V,\,n_i}, \qquad (10)$$

the substitutions of the characteristic group, as summarized in the characteristic array (8), yield:

$$\begin{aligned}
\left(\frac{\partial |T|}{\partial V}\right)_{S,\,n_i} &= -\left(\frac{\partial |P|}{\partial S}\right)_{V,\,n_i},\\
-\left(\frac{\partial |V|}{\partial S}\right)_{P,\,n_i} &= -\left(\frac{\partial |T|}{\partial P}\right)_{S,\,n_i},\\
-\left(\frac{\partial |S|}{\partial P}\right)_{-T,\,n_i} &= +\left(\frac{\partial |V|}{\partial T}\right)_{-P,\,n_i},\\
\left(\frac{\partial |P|}{\partial T}\right)_{-V,\,n_i} &= +\left(\frac{\partial |S|}{\partial V}\right)_{-T,\,n_i},\\
\left(\frac{\partial |S|}{\partial V}\right)_{-T,\,n_i} &= +\left(\frac{\partial |P|}{\partial T}\right)_{V,\,n_i},\\
-\left(\frac{\partial |P|}{\partial S}\right)_{-V,\,n_i} &= +\left(\frac{\partial |T|}{\partial V}\right)_{-S,\,n_i},\\
-\left(\frac{\partial |T|}{\partial P}\right)_{S,\,n_i} &= -\left(\frac{\partial |V|}{\partial S}\right)_{-P,\,n_i},\\
\left(\frac{\partial |V|}{\partial T}\right)_{P,\,n_i} &= -\left(\frac{\partial |S|}{\partial P}\right)_{T,\,n_i}.
\end{aligned} \qquad (11)$$

The eight equations of this set are readily shown to be f_1^1-equations in standard form. The set is seen to contain only four distinct f_1^1-equations, i.e., it constitutes a four membered f_1^1-family, to which moreover (9) belongs. This family may if desired be obtained in the usual form by dropping from the first four equations of the set (11) the absolute value signs and the minus signs in the subscripts. It can be verified that the three remaining standard forms of (9) as well as the three other members of the f_1^1-family in question in any of their standard forms all yield the same family.

F. Survey of Some f_1^1-Families of Physical Interest

Any f_1^1-equation can be treated by the same method as Eq. (9) above. The results for a number of f_1^1-equations of physical interest[3] are summarized below. In every case the theorems on which the method is based have been confirmed.

[3] For proof that the equations to be considered are f_1^1-equations, i.e., for their derivation from the basic equations (without the basic assumption (ii) above) see E. A. Guggenheim, *Modern Thermodynamics by the Methods of Willard Gibbs*, Methuen, London, 1933.

1. The basic families

The basic Eqs. (2) are found to belong to the following four membered f_1^1-family:

$$\begin{aligned} E&=H-VP, \quad F=A+PV, \\ H&=F+ST, \quad A=E-TS, \end{aligned} \tag{12}$$

and the basic Eq. (3) yields the four general Gibbsian equations of the system:

$$\begin{aligned} dE&=-PdV+TdS+\sum_i \mu_i dn_i, \\ dH&=\ TdS+VdP+\sum_i \mu_i dn_i, \\ dF&=\ VdP-SdT+\sum_i \mu_i dn_i, \\ dA&=-SdT-PdV+\sum_i \mu_i dn_i. \end{aligned} \tag{13}$$

The f_1^1-families (12) and (13) may be called the "basic families."

2. Partial derivatives of the characteristic functions

(i) *With respect to* V, S, P, T. The equation:

$$(\partial F/\partial T)_{P,\ n_i}=-S \tag{14}$$

yields an f_1^1-family of eight members, which may be written in condensed form as:

$$\begin{aligned} \left(\frac{\partial E}{\partial V}\right)_{S,\ n_i} &= -P=\left(\frac{\partial A}{\partial V}\right)_{T,\ n_i}, \\ \left(\frac{\partial H}{\partial S}\right)_{P,\ n_i} &= \ T=\left(\frac{\partial E}{\partial S}\right)_{V,\ n_i}, \\ \left(\frac{\partial F}{\partial P}\right)_{T,\ n_i} &= \ V=\left(\frac{\partial H}{\partial P}\right)_{S,\ n_i}, \\ \left(\frac{\partial A}{\partial T}\right)_{V,\ n_i} &= -S=\left(\frac{\partial F}{\partial T}\right)_{P,\ n_i}. \end{aligned} \tag{15}$$

(ii) *With respect to* n_i. The equation:

$$(\partial F/\partial n_i)_{P,\ T,\ n_i'}=\mu_i, \tag{16}$$

where the subscript n_i' indicates the constancy of all the n_i except the particular one with respect to which the differentiation is carried out, yields the four membered f_1^1-family:

$$\left.\begin{aligned} &(\partial E/\partial n_i)_{V,\ S,\ n_i'} \\ &(\partial H/\partial n_i)_{S,\ P,\ n_i'} \\ &(\partial F/\partial n_i)_{P,\ T,\ n_i'} \\ &(\partial A/\partial n_i)_{T,\ V,\ n_i'} \end{aligned}\right\}=\mu_i. \tag{17}$$

The particularly simple relations of the families (15) and (17) to the geometrical Figs. 1 are worth noting.

3. The Gibbs-Helmholtz type

Either one of the Eqs. (1) yields the following eight membered f_1^1-family:

$$\begin{aligned} E&=H-P\left(\frac{\partial H}{\partial P}\right)_{S,\ n_i}, & A&=F-P\left(\frac{\partial F}{\partial P}\right)_{T,\ n_i}, \\ H&=F-T\left(\frac{\partial F}{\partial T}\right)_{P,\ n_i}, & E&=A-T\left(\frac{\partial A}{\partial T}\right)_{V,\ n_i}, \\ F&=A-V\left(\frac{\partial A}{\partial V}\right)_{T,\ n_i}, & H&=E-V\left(\frac{\partial E}{\partial V}\right)_{S,\ n_i}, \\ A&=E-S\left(\frac{\partial E}{\partial S}\right)_{V,\ n_i}, & F&=H-S\left(\frac{\partial H}{\partial S}\right)_{P,\ n_i}. \end{aligned} \tag{18}$$

4. Partial derivatives of μ_i with respect to V, S, P, T

The equation:

$$(\partial \mu_i/\partial T)_{P,\ n_i}=-(\partial S/\partial n_i)_{T,\ P,\ n_i'} \tag{19}$$

is found to yield an f_1^1-family of eight members.

5. The equations of the type:

$$(\partial E/\partial V)_{T,\ n_i}=T(\partial P/\partial T)_{V,\ n_i}-P. \tag{20}$$

This equation, useful in the theory of constant volume thermometry, is found to belong to an eight membered f_1^1-family.

6. The equations of the type:

$$\left(\frac{\partial T}{\partial V}\right)_{E,\ n_i}=P-T\left(\frac{\partial P}{\partial T}\right)_{V,\ n_i}\Big/\left(\frac{\partial E}{\partial T}\right)_{V,\ n_i}. \tag{21}$$

These equations are found to constitute an eight membered f_1^1-family.

7. The equations of the type:

$$(\partial H/\partial T)_{P,\ n_i}=T(\partial S/\partial T)_{P,\ n_i}. \tag{22}$$

This equation, important in the determination of entropy from heat capacity, yields an f_1^1-family of eight members.

8. The equations of the type:

$$(\partial H/\partial T)_{P,\ n_i}-(\partial E/\partial T)_{V,\ n_i}$$
$$=T(\partial P/\partial T)_{V,\ n_i}\cdot(\partial V/\partial T)_{P,\ n_i}. \quad (23)$$

Eq. (23) is the familiar relation between the two heat capacities written as an f_1^1-equation. It is found to belong to an f_1^1-family of four members.

9. Remark on the number of members in an f_1^1-family

The number of members in an f_1^1-family evidently cannot exceed eight. All the families mentioned above have either eight or four members. These are however not the only possibilities because the two f_1^1-equations:

$$E-F=TS-PV, \quad (24)$$

$$E-H+F-A=0, \quad (25)$$

are seen to belong to f_1^1-families of two members and one member, respectively. Some theorems concerning the number of members in a family will be given in a later paper (communication II).

10. Concluding remarks

It is evident that the method here described greatly increases the number of fundamental equations which are readily available. The method can however scarcely be regarded as an alternative to P. W. Bridgman's[4] condensed summary of differential coefficients because it differs too much from the latter both in requirements and in results. It may perhaps find some use as a supplement to the method of Bridgman.

More valuable than the proliferation of formulae seems the way in which the above considerations reveal the symmetry of the equations of thermodynamics, a keen sense of which is helpful to any student of the subject.

The author is indebted to Dr. C. F. Luther of the Department of Mathematics, Stanford University, for much valuable advice.

[4] P. W. Bridgman, Phys. Rev. [2] **3**, 273 (1914); see also G. N. Lewis and M. Randall, *Thermodynamics, etc.* pp. 163–165 (1923).

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The Compressibility of Solutions of Three Amino Acids

P. W. BRIDGMAN AND R. B. DOW, *Research Laboratory of Physics, Harvard University*

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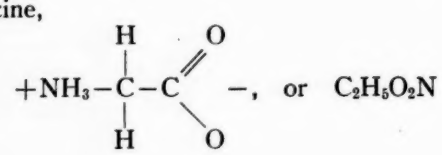
The compressibility of aqueous solutions of glycine, α-amino butyric acid, and ε-amino caproic acid have been measured over the concentration range up to 2.5 N at 25° and 75°C and up to a maximum pressure of 8000 kg/cm². The results are exhibited in tables giving the volume in cm³ as a function of pressure, temperature, and concentration of that amount of solution which contains one gram of water, and in figures showing the apparent molal volume at 25° as a function of pressure and concentration. The general character of the results is complicated; the most striking result is that at low pressures the apparent compressibility of the acid in solution is positive, which is opposite in sign from all other known solutes. A connection is probable with the high dielectric constant. Other qualitative aspects of the phenomena are discussed.

A NUMBER of the physical properties of that very interesting group of highly polar substances known as Zwitterions have been studied during the last few years. Dr. E. J. Cohn,[1] of the Harvard Medical School, who has contributed so much to our knowledge of these substances suggested that a study of the compressibility at high pressures might be expected to be of interest, and he very kindly undertook to provide the materials from his highly purified stock. It was desired to study the compressibility over as wide a range of concentration as possible, which demanded that the substance have high solubility, and also over as wide a range of composition as possible. The following representatives of the class of Zwitterions were therefore

[1] Edwin J. Cohn, *Die Physikalische Chemie der Eiweisskörper*, Ergebnisse der Physiologie **33**, 782–882 (1931).

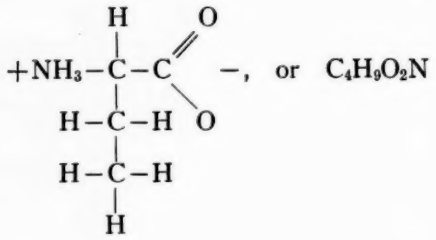
selected with Dr. Cohn's advice, as best meeting these requirements:

Glycine,



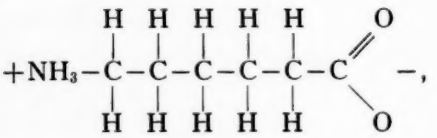
$C_2H_5O_2N$

α−amino, butyric acid,



$C_4H_9O_2N$

ϵ−amino caproic acid,



or $C_6H_{13}O_2N$.

The method of measurement was the sylphon method, which has already been used in determining the compressibility of some 50 different liquids, and which has been described in detail elsewhere.[2] The pressure range was limited by the solubility of the acid. The solubility of these three acids decreases under pressure, so that if pressure is pushed high enough, separation into two phases, solution and solid acid, takes place. Precipitation of the solid is in practice an irreversible process, because, although on reducing pressure re-solution will take place and the solution will eventually become homogeneous again by diffusion, the process of homogenization after precipitation is so very slow because of high viscosity that it is impossible to wait for completion of the process. The upper pressure limit in the following was 8000 kg/cm², and in a number of cases the limit was lower. No attempt was made to get exact values for the effect of pressure on solubility, and the pressure limits of the tables should not be taken as having any significance in this regard. Sometimes 8000 kg may have exceeded the solubility limit, but precipitation failed to take place because of supersaturation phenomena, while at other times the saturation limit doubtless was not reached, but the pressure limit may have been set instead by incidental considerations peculiar to that particular experiment. No runs were accepted in computing the final results in which precipitation was known to have occurred; the criterion was that the points obtained with decreasing pressure failed to coincide with those obtained with increasing pressure.

The compositions studied of glycine were: 0.5, 1.0, 1.5, 2.0 and 2.5 molal; of α-amino butyric acid 0.5 and 1.5 molal, and of ϵ-amino caproic acid 0.5, 1.0, 1.5, 1.75, 2.0, and 2.5 molal. The concentration 1.75 molal was at first omitted from the ϵ-amino caproic series. On calculating and plotting the results such surprising departures from linearity appeared that a check was imperative, although the method had shown itself capable of high precision when used before. Accordingly the runs at 1.5 and 2.0 molal on ϵ-amino caproic acid were repeated with freshly prepared material, and the new composition 1.75 molal was interpolated. The results for this new composition lay within the error of the repetition on the curve which had been previously drawn to represent the results previously obtained, thus checking the reality of the nonlinear effects. The order of reproducibility of the results can be estimated from the fact that the average departure from the mean of all the readings of the relative volume was 0.0010, and the maximum departure, which occurred at the maximum pressure 8000, was 0.0030. This agreement is not as good as has usually been obtained with other liquids. The irregularities were not explained with complete satisfaction, but were doubtless connected with the material itself. The solutions were usually found to be slightly discolored when the sylphon was emptied at the end of a pressure run, and the conventional chemical tests showed the presence of some iron after the runs, although the sylphon was made entirely of brass, copper, and solder, and the same test

[2] P. W. Bridgman, Proc. Am. Acad. Sci. **66**, 185 (1931); **67**, 1 (1932); **68**, 1 (1933).

TABLE I. *Volume of glycine solutions.*

Pressure kg/cm²	Pure Water Vol. of 1 g 25°C	75°C	0.5 Molal Vol. of {1 g water 0.03847 g acid 25°C	75°C	1.0 Molal Vol. of {1 g water 0.07874 g acid 25°C	75°C	1.5 Molal Vol. of {1 g water 0.12097 g acid 25°C	75°C	2.0 Molal Vol. of {1 g water 0.16523 g acid 25°C	75°C	2.5 Molal Vol. of {1 g water 0.2122 g acid 25°C	75°C
1	1.0029		1.0255		1.0490		1.0747		1.1015		1.1307	
250	.9929		1.0148		1.0370		1.0635		1.0909		1.1191	
500	.9834	1.0055	1.0050	1.0300	1.0254	1.0530	1.0533	1.0822	1.0807	1.1051	1.1081	1.1356
750	.9741	.9969	.9962	1.0214	1.0149	1.0426	1.0437	1.0723	1.0713	1.0954	1.0978	1.1254
1000	.9657	.9885	.9880	1.0130	1.0050	1.0324	1.0344	1.0628	1.0620	1.0860	1.0880	1.1152
1500	.9494	.9729	.9726	.9967	.9878	1.0143	1.0171	1.0444	1.0442	1.0683	1.0705	1.0969
2000	.9355	.9578	.9593	.9824	.9722	.9981	1.0016	1.0277	1.0279	1.0528	1.0551	1.0808
2500	.9232	.9444	.9467	.9689	.9583	.9836	.9873	1.0129	1.0141	1.0394	1.0409	1.0664
3000	.9119	.9325	.9352	.9566	.9451	.9701	.9739	.9993	1.0006	1.0258	1.0278	1.0535
4000	.8918	.9117	.9153	.9359	.9227	.9460			.9785	1.0039	1.0045	1.0296
5000	.8739	.8938	.8984	.9187	.9028	.9258			.9596	.9845	.9838	1.0089
6000	.8578	.8777	.8842	.9039	.8848	.9079			.9424	.9666		.9901
7000	.8428	.8698		.8905		.8921				.9501		.9736
8000	.8289	.8509		.8784		.8780				.9350		.9587

had shown no iron before the run. However, the original material from which the acid was purified was known to contain some iron, so that it is perhaps possible that iron may have been initially present in the solution in a form undetectible by the conventional test and then transformed by pressure into a detectible form. Any irregularities of this nature are, however, entirely too small to change appreciably the results when shown on the scale of magnitude of the figures, and any conclusions to be drawn here will not be affected. But a complete thermodynamic discussion of the properties of solutions under pressure, such for example as that recently given by Adams and Gibson[3] at the Geophysical Laboratory in deducing the solubility limits, demands that differentiations be performed with respect to the various variables, pressure, temperature and composition. Care should be used in subjecting the data of this paper to operations of this sort, and conclusions drawn from such operations should be carefully examined.

The results were computed according to methods already described, which give immediately the relative volumes, the volume of each solution at 25° at atmospheric pressure being taken as unity. For purposes of discussion the results may be presented in many ways, depending on the use to which they are to be put. It has seemed that perhaps the best general idea of the nature of the results is given by tabulating the volumes, as function of pressure, temperature and concentration, of that amount of solution which contains one gram of water. In comparing solutions of different strengths the water factor thus remains constant, and the difference is due to the different amounts of acid. The results are presented in this form in Table I for glycine, Table II for α-amino butyric acid, and Table III for ε-amino caproic acid. In recalculating the results for presentation in this form in the tables the densities of the solutions at 25° and atmospheric pressure and the molecular weights were involved. It is possible to reconstruct the densities from the values given in the tables, but for convenience they are given here explicitly; they were originally determined in Dr. Cohn's laboratory, and are still partially unpublished.

TABLE II. *Volume of α-amino butyric acid solutions.*

Pressure kg/cm²	Pure Water Vol. of 1 g 25°C	75°C	0.5 Molal Vol. of {1 g water 0.0537 g acid 25°C	75°C	1.5 Molal Vol. of {1 g water 0.1751 g acid 25°C	75°C
1	1.0029		1.0425		1.1324	
250	.9929		1.0301		1.1213	
500	.9834	1.0055	1.0189	1.0449	1.1109	1.1394
750	.9741	.9969	1.0094	1.0351	1.1016	1.1298
1000	.9657	.9885	1.0009	1.0263	1.0933	1.1206
1500	.9494	.9729	.9863	1.0108	1.0784	1.1038
2000	.9355	.9578	.9732	.9970	1.0649	1.0894
2500	.9232	.9444	.9613	.9841	1.0518	1.0764
3000	.9119	.9325	.9504	.9725	1.0385	1.0635
4000	.8918	.9117	.9301	.9527	1.0141	1.0387
5000	.8739	.8938	.9115	.9339		
6000	.8578	.8777	.8968	.9172		
7000	.8428	.8698	.8834			
8000	.8289	.8509	.8714			

Densities at 25°C.

Glycine		α-amino butyric		ε-amino caproic	
0.5 M	1.01268	0.5 M	1.01075	0.5 M	1.01041
1.0	1.02822	1.5	1.03767	1.0	1.02338
1.5	1.04303			1.5	1.03620
2.0	1.05775			1.75	1.04221
2.5	1.07181			2.0	1.04822
				2.5	1.06016

[3] L. H. Adams and R. E. Gibson, J. Am. Chem. Soc. **52**, 4252 (1930). R. E. Gibson and L. H. Adams, ibid. **55**, 2679 (1933). L. H. Adams, ibid. **53**, 3769 (1931); **54**, 2229 (1932).

TABLE III. *Volume of ε-amino caproic acid solutions.*

Pressure kg/cm²	Pure Water Vol. of 1 g		0.5 Molal Vol. of {1 g water 0.0694 g acid		1.0 Molal Vol. of {1 g water 0.1469 g acid		1.5 Molal Vol. of {1 g water 0.2342 g acid		1.75 Molal Vol. of {1 g water 0.2823 g acid		2.0 Molal Vol. of {1 g water 0.3336 g acid		2.5 Molal Vol. of {1 g water 0.4476 g acid	
	25°C	75°C	25°C	75°C	25°C	75°C	25°C	75°C	25°C	75°C	25°C	75°C	25°C	75°C
1	1.0029		1.0583		1.1207		1.1913		1.2307		1.2723		1.3655	
250	.9929		1.0473		1.1073		1.1818		1.2204		1.2610		1.3542	
500	.9834	1.0055	1.0369	1.0632	1.0946	1.1281	1.1726	1.1967	1.2106	1.2370	1.2502	1.2822	1.3435	1.3712
750	.9741	.9969	1.0274	1.0537	1.0827	1.1157	1.1637	1.1873	1.2018	1.2281	1.2407	1.2706	1.3336	1.3607
1000	.9657	.9885	1.0181	1.0448	1.0721	1.1043	1.1557	1.1784	1.1937	1.2196	1.2305	1.2607	1.3240	1.3506
1500	.9494	.9729	1.0012	1.0278	1.0537	1.0836	1.1403	1.1629	1.1790	1.2047	1.2130	1.2419	1.3086	1.3324
2000	.9355	.9578	.9857	1.0118	1.0381	1.0663	1.1267	1.1486	1.1658	1.1900	1.1973	1.2248	1.2914	1.3156
2500	.9232	.9444	.9721	.9972	1.0237	1.0507	1.1143	1.1356	1.1535	1.1764	1.1838	1.2098	1.2763	1.3006
3000	.9119	.9325	.9595	.9840	1.0099	1.0363	1.1026	1.1237	1.1425	1.1644	1.1698	1.1954	1.2646	1.2870
4000	.8918	.9117	.9368	.9616	.9849	1.0108	1.0822	1.1022	1.1225	1.1432	1.1463	1.1713	1.2406	1.2627
5000	.8739	.8938		.9432	.9633	.9889	1.0642	1.0829	1.1044	1.1249	1.1253	1.1498	1.2206	1.2417
6000	.8578	.8777		.9275	.9446	.9688	1.0490	1.0663	1.0884	1.1084	1.1057	1.1301	1.2021	1.2226
7000	.8428	.8698			.9269	.9509	1.0348	1.0518	1.0732	1.0934	1.0872	1.1121		1.2065
8000	.8289	.8509			.9112	.9346	1.0218	1.0391	1.0572	1.0797	1.0697	1.0940		1.1919

The molecular weights used in the calculations were, respectively, 75.047, 103.077 and 131.108.

The "apparent molal volume" of the acid in solution may be readily obtained from the data in the tables. The apparent molal volume is defined as the difference between the volume of that amount of solution in which is dissolved one gram molecule of the acid and the volume in the pure state of the amount of water contained in the same solution. To illustrate the method of calculation, the apparent molal volume of glycine in 0.5 molal solution at 25° is obtained by subtracting the volume of pure water listed in column 2 of Table I from the volume of the 0.5 M solution listed in column 4, and multiplying the difference by 75.047/0.03847. The apparent molal volumes at 25°, calculated in this way, of the three solutions are shown in Figs. 1 to 3 as a function of pressure.

If there were no interaction between the water and the acid in the solution, that is, if our calculation of the apparent molal volume had been applied not to the solution but to a compound system containing pure water and the solid acid, the curves of apparent molal volume against pressure would have been the same for all concentrations, and would fall smoothly with pressure, the slope being a measure of the compressibility of the solid. The failure of the curves to possess this simple property is due to the interaction between water and acid in the solution.

The state of affairs in the solution as revealed by these curves is most complicated, so complicated that it would be hopeless, in the present condition of the theory of solutions, to attempt a detailed explanation of all the features; all that will be attempted will be a qualitative comment on a couple of the most striking features.

In one important particular the behavior of these three acid solutions under pressure is sharply different from that of all other solutions hitherto investigated. The curve of apparent molal volume against pressure of solutions of electrolytes and those few non-electrolytes which have been measured rises over the entire range of pressure, except possibly in a very few cases at the highest pressures. This result for ordinary electrolytes at first appears paradoxical, for it means that the apparent molal compressibility of the dissolved substance, defined as the negative pressure derivative of the apparent molal volume is negative. This paradoxical result receives qualitative explanation in Tammann's theory of solutions, which is that any aqueous solution behaves approximately like pure water under some higher pressure. The essential role of the dissolved substance according to this picture is merely to increase the internal pressure of the solvent water by a fixed amount; except for this the dissolved substance acts as an inert addendum to the system with constant volume. The negative apparent molal compressibility of the dissolved substance is a consequence of this hypothesis, as a little algebra shows at once, utilizing the fact that the compressibility of water decreases with increasing pressure. A second approximation would add to the compressibility of the water at a higher pressure the compressibility of the dissolved substance, but this is small for such typical solutes as NaCl,

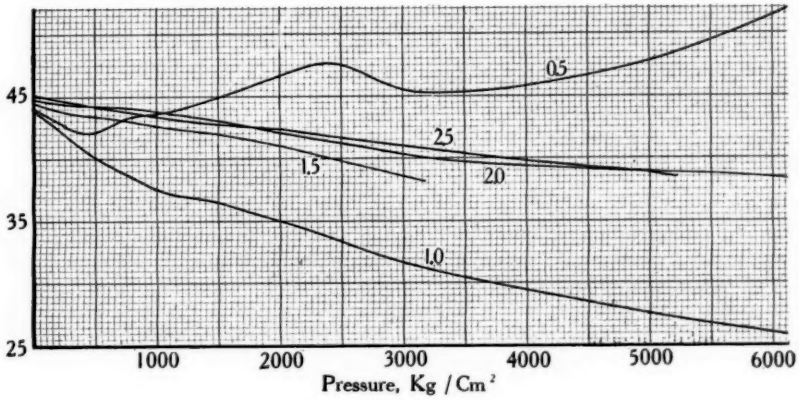


FIG. 1. The apparent molal volumes at 25°C of glycine as a function of pressure. The figures on the curves give the molal concentrations.

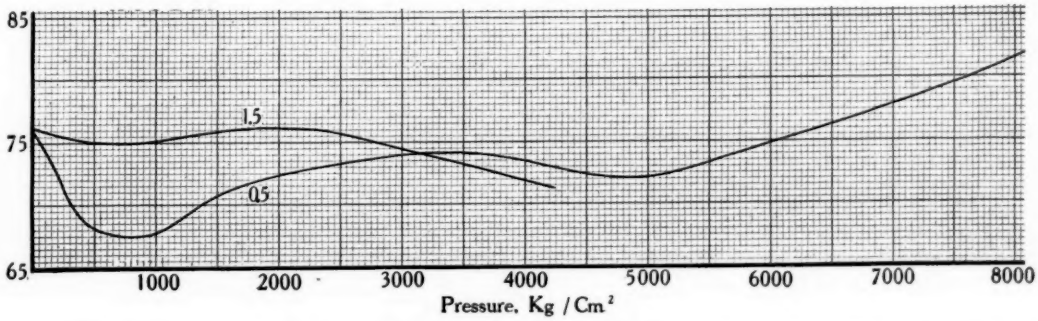


FIG. 2. The apparent molal volumes at 25°C of α-amino butyric acid as a function of pressure. The figures on the curves give the molal concentrations.

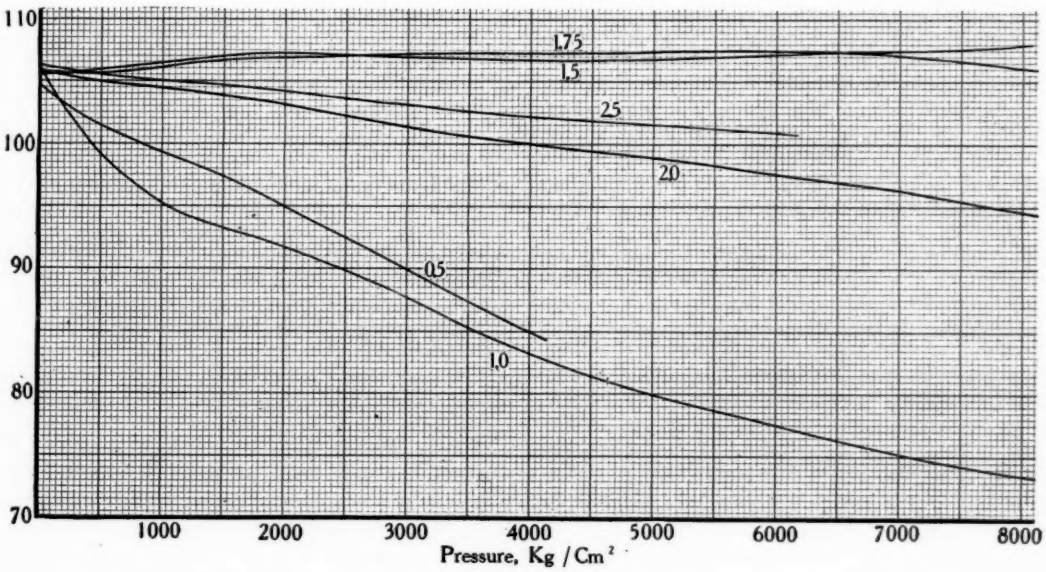


FIG. 3. The apparent molal volumes at 25°C of ϵ-amino caproic acid as a function of pressure. The figures on the curves give the molal concentrations.

and the situation is dominated by the water.

Contrasted to this almost universal behavior is the behavior of these solutions of Zwitterions. The initial slopes at practically all concentrations of the curves of apparent volume against pressure are negative, that is, the apparent compressibility of the dissolved substance is positive. Expressed in terms of Tammann's theory this would mean that the effect of the dissolved substance is here to *decrease* the internal pressure of the water, instead of to increase it. It seems not unreasonable that such a decrease of internal pressure is to be correlated with the dielectric behavior of these solutions. It has been established by the work of Wyman[4] and others that the dielectric constant of a solution of a Zwitterion in water is higher than the already high dielectric constant of the water. An increase of dielectric constant means a decrease of the intensity of the forces arising from electric charges, and hence a diminution of that part of the internal pressure arising from forces between electric charges separated by distances so great that the intervening medium acts as an approximately homogeneous medium with the mean dielectric constant. This, however, can be only one of the features in the situation, for it is known that solutions of urea, which are unusual in that they increase the dielectric constant of water, are normal in that the urea in solution has a negative, although abnormally low, apparent molal compressibility. Furthermore, the second approximation, which takes account of the compressibility of the dissolved substance, may reasonably be expected to be important when the dissolved molecule is as large as it is here. Unfortunately the compressibility of none of these acids has been determined in the solid state; we may guess that the order of magnitude of the compressibility would not be far different from that of a number of other solid organic compounds, which lose about 1.5 percent in volume at 1000 kg/cm^2. An effect of this magnitude would account for a large part of the initial slope of the curves for the more concentrated solutions.

[4] Jeffries Wyman, Jr., Phys. Rev. **35**, 623 (1930); J. Biol. Chem. **90**, 434 (1931); J. Am. Chem. Soc. **56**, 536 (1934). Jeffries Wyman, Jr., and T. L. McMeekin, J. Am. Chem. Soc. **55**, 908, 915 (1933).

At low pressures the behavior of the more concentrated solutions approaches more closely to that of normal electrolytes than does that of the weaker solutions, that is, the apparent molal compressibility of the more concentrated solutions is less strongly positive. At concentrations beyond 1.0 molal there is a striking tendency for the curves of apparent molal volume to become relatively independent of concentration, and in fact to approach the behavior of a system in which there is no interaction between water and acid. But in the concentration range between 0 and 1.0 molal the behavior at constant pressure as a function of concentration is evidently highly complicated. In particular, the volume is very far from being a linear function of $c^{\frac{1}{2}}$, and in fact this relation fails even at atmospheric pressure, although the relation is satisfied for practically all other substances. Neither is apparent molal volume any more approximately a linear function of c. Scatchard and Kirkwood[5] have recently verified the conclusion that in dilute solutions the effect of a Zwitterion should be proportional to the first power of the concentration rather than to its square root.

Resemblances would be expected between the behavior of glycine and α-amino butyric acid because of the resemblances of structure. A glance at the structural formulas shows that the electrically active parts of the two molecules are identical, α-amino butyric acid differing from glycine only in that it carries attached to it an inert tail; that is, the polar moments of these two acids must be nearly the same. At the 0.5 molal concentration the similarity in the behavior of these two substances is striking; both curves have a sharp initial drop, a rise to a maximum, followed by a drop to a second minimum, and ultimately at high pressures a continued rise, which means that the apparent molal compressibility ultimately becomes negative, which is typical of other substances. The curves at 1.5 molal, the only other concentration measured for the α-amino butyric acid, are much more featureless than the curves for 0.5 molal, and differ no more in absolute terms. Contrasted with these, the moment of ϵ-amino caproic acid

[5] G. Scatchard and J. G. Kirkwood, Phys. Zeits. **33**, 297 (1932).

must be very materially larger, as shown by its structure, and one would therefore be prepared for qualitative differences in behavior. The most marked difference in behavior is seen to be at the lowest concentration.

Another line of comparison suggests itself. Glycine differs from α-amino butyric acid only in the presence of a C_2H_4 group. The difference of the molal volumes of corresponding solutions may therefore be described as the contribution to the volume of C_2H_4, and if the comparison is made at different pressures, the volume of the C_2H_4 group is obtained as a function of pressure. A simple calculation shows that in 0.5 M solution the volume of the C_2H_4 group decreases from 31.91 at atmospheric pressure to 28.41 at 3000 kg/cm², whereas in 1.5 M solution it *increases* from 31.70 at atmospheric to 36.05 at 3000. Similar calculations may be made for other groups of compounds. Thus from the compressibility of the propyl and amyl halides,[6] the volume of the C_2H_4 group may be obtained as a function of pressure by subtraction. It turns out that in these compounds the volume decreases with pressure by roughly the same amount in the chloride, bromide and iodide, which is as one might expect, and surprisingly enough the volumes are about the same as in the 0.5 M solution. From this point of view the 0.5 M solution is therefore more nearly normal than the 1.5 M solution, although the apparent volume curve against pressure of the 1.5 M solution is much more regular than that of the 0.5 M solution.

A study of the thermal expansion discloses only complications which are probably too great to attempt to unravel at present; such complications would be expected in view of the complications already found with respect to pressure. In very broad comment, the thermal expansion shows a very much smaller tendency to become less at high pressures than it does for normal organic substances; this is a property of the water in the solution which was already known.

[6] P. W. Bridgman, Proc. Am. Acad. Sci. **68**, 1 (1933).

Effects as complicated as these obviously demand something more specific in the way of explanation than such general considerations as, for example, the internal pressure in the solution. In fact, from the point of view of internal pressure the variety and magnitude of the effects is very surprising. Thus, to take an extreme case, the initial slope of the curve of apparent volume of 0.5 M α-amino butyric acid has the largest negative value to be found anywhere in the series. A consideration of numerical magnitudes shows that this means, according to Tammann's picture, that the water in the solution is under a negative pressure of something of the order of 1000 kg/cm². But the internal pressure in water under normal conditions is of the order of 10,000 or 20,000 kg/cm², so that the total internal pressure of the 0.5 M solution is little affected by the dissolved acid. External pressures would not be expected to produce important changes in the properties of such solutions until they become comparable in magnitude with the internal pressures already existing, or in this case, until a pressure is reached comparable with 10,000 kg/cm². But actually an external pressure of only 800 kg/cm² acting on this solution reverses the sign of the apparent molal compressibility.

Perhaps something in the nature of specific clustering or hydration effects, involving the possibility of multiple types of approximate order, would be competent to explain the complicated effects. But such effects must be surprisingly sensitive to changes of pressure which would be judged to be comparatively slight from the point of view of other phenomena.

The great complication of these pressure effects suggests that an experimental examination of other phenomena in these solutions might be profitably undertaken. For example, measurements might well be made of the effect of pressure on solubility and on the dielectric constants, on the compressibility of non-aqueous solutions and of solutions of other acids in the series, and of the compressibility of the solid phases of the pure acids.

The Vitreous State

GUNNAR HÄGG, *Institute of General and Inorganic Chemistry of the University, Institute of Metallography, Stockholm, Sweden*

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The tendency of glass forming substances to supercooling is discussed in connection with the existence of large or irregular groups in the melts of such substances. If the size of these groups makes their direct addition to the crystal lattice difficult, and if the forces within them are so strong as to prevent a rapid disintegration of the groups, the melt will tend to supercooling and glass formation. In the inorganic glasses consisting of oxides of metalloids or the corresponding acids or salts, the formation of large or irregular groups is caused by the strong tendency of these metalloids to coordinate oxygen in a definite way. If the number of available oxygen atoms is smaller than necessary for the formation of discrete polyhedral groups with the required coordination, the polyhedra will be linked together sharing oxygen atoms. The resulting groups will delay crystallization and thus cause the formation of glass.

TWO years ago Zachariasen[1] published a paper on the atomic arrangement in glass, where he put forth some new conceptions regarding this matter. He considers mainly oxide glasses and is of the opinion that in a glass of an oxide A_mO_n, the atoms A are surrounded by oxygen polyhedra of the same sort as in a crystal A_mO_n. The coordination number of the atoms A is, consequently, the same as in a crystal. The difference between glasses and crystals lies in the different linking together of the polyhedra. A crystal is built up by polyhedra linked together and arranged in a quite definite way so that a lattice of a certain symmetry and periodicity is formed. In the corresponding glass, polyhedra of the same sort are linked together in a more random way, although certain requirements must be fulfilled. Zachariasen states these requirements as follows: (1) an oxygen atom is linked to not more than two atoms A; (2) the number of oxygen atoms surrounding atoms A must be small; (3) the oxygen polyhedra share corners with each other, not edges or faces; (4) at least three corners in each oxygen polyhedron must be shared. Such a random network of polyhedra, lacking symmetry and periodicity, would give a glass isotropic properties and Zachariasen thinks that the optical clearness of glasses is explained by the continuous network in just the same manner as the optical clearness of crystals is accounted for. A network of this kind would possess an energy only slightly different from that of the crystal which would account for the small tendency of a glass to crystallize.

Previous to Zachariasen's paper the general opinion was that a glass consisted of crystallites, possessing the same lattice as the corresponding stable crystalline phase. These crystallites were orientated in a random way, which would explain the isotropic qualities of a glass. The crystallites were so small that no sharp x-ray interferences could be obtained but their dimensions were still large enough to give to the molten glass a very high viscocity.

The last-mentioned theory has never been put forth in any precised form and the causes why one substance is more liable to form a glass than another have never been explained in the light of this theory.

The author is of the opinion that Zachariasen's theory cannot furnish an explanation of the vitreous state in general and hardly even of the state of the oxide glasses in general. Zachariasen's theory is only adaptable to cases where the oxygen polyhedra can form a three-dimensional network. As is well known, the crystal lattice of large groups of silicates contains one-dimensional chains or two-dimensional sheets of oxygen tetrahedra and it is hard to see how the atomic arrangement in the corresponding glasses in these cases could be explained according to Zachariasen. One could assume that the chains or sheets also exist in the glasses, but without symmetry and periodicity in the linking of the polyhedra. However, such an assumption would give rise to anisotropic properties in the glass. These could be avoided if the chains or sheets loose their linear or plane form, but the twisting or bending in this case can only take place if they

[1] W. H. Zachariasen, J. Am. Chem. Soc. **54**, 3841 (1932).

break into comparatively small fragments. This would import the abandoning of Zachariasen's theory, and the introduction of a sort of "crystallite" theory. Another way would be to assume that a three-dimensional linking of the polyhedra takes place in the glass, even if the corresponding crystal structure contains polyhedra linked together in chains or sheets. In most cases this would make a change of the coordination number of the atoms A necessary, and it can be said with certainty that such differences between the atomic arrangements in crystals and glass would give rise to energy differences between the two states too large to explain the small crystallization velocity of the glass.

It is obvious that although different kinds of glass have many properties in common, their internal structure must differ very much from one case to another. So many different types of substances can exist in the vitreous state that only the most general characteristics of the state can serve as starting points for a discussion. Certainly the most useful characteristic is the conception of glasses as being supercooled liquids. A probable consequence of this is that all substances should be able to form glass if they could be cooled from the liquid state rapidly enough (Tammann), and the question then arises why certain substances are so disposed to supercooling, others not. The following comparison and discussion of the probable mechanism of the melting and solidifying of two different types of salts seems to throw light upon one important cause of the supercooling tendency.

The melting point of an ordinary salt, whose lattice is built up by single ions or separate charged groups of atoms (radicals), means the temperature at which the bonds between the ions loosen. The bonds holding the atoms of a radical together are, however, generally much stronger than the ionic bonds, and the consequence will be that the radicals will still exist in the melt.* When, for example, KNO_3 melts, the bonds existing in the crystal between the K^{+1} and the $(NO_3)^{-1}$ ions break up but the bonds within the $(NO_3)^{-1}$ ion will not be affected, and these groups certainly exist in the melt. When the temperature is lowered again and crystallization begins at the freezing point, this process can proceed very rapidly. The growing of a crystal lattice implies that the mobile ions which are to be found in the melt all around the crystal are added to the latter. These ions are only drawn out of the relatively weak field of interionic forces existing in the melt, and are added directly in definite places of the lattice.

On the other side the melting of for example crystals of calcium metaborate, $Ca(BO_2)_2$, and the subsequent cooling of the melt will afford quite a different mechanism. The crystal structure of this salt has been determined by Zachariasen and Ziegler.[2] The boron atom has a strong tendency to coordinate three oxygen atoms and this can be effected in this case only if the oxygen triangles surrounding the boron atoms have corners in common. In this way, straight, unlimited chains of oxygen triangles with boron atoms in their centers are formed. These chains having the composition $\infty(BO_2)$ (∞ means without limit throughout the crystal), are arrayed parallel to each other. They can without doubt be considered as unlimited radicals $\infty(BO_2)^{-1}$, within which the atoms are kept together by comparatively strong bonds. The lattice as a whole is built up by these large radicals and the Ca^{+2} ions. When crystals of $Ca(BO_2)_2$ melt, the ionic bonds between Ca^{+2} and chain radicals $\infty(BO_2)^{-1}$ break, but chains will still exist in the melt owing to the strong bonds within them. However, they cannot maintain their original length now when they are not supported in the rigid lattice but certainly break into smaller parts, and are probably also more or less bent and twisted. The melt therefore consists of Ca^{+2} ions and chain fragments $n(BO_2)^{-1}$ of different lengths. The latter cause the high viscosity of the $Ca(BO_2)_2$ melt. Their length certainly decreases when the temperature of the melt is raised still more.

If now the temperature of the melt in question is lowered, a point is reached, where a tendency

* The author will not here enter into the question of the nature of the bonds keeping together the atoms of the radicals discussed here and in the following. They are probably in some cases of a more or less homopolar character but in this connection their main characteristic is that they are stronger than the forces existing outside the radical.

[2] W. H. Zachariasen and G. E. Ziegler, Z. Krist. **83**, 354 (1932).

to lattice formation sets in. But here the addition of groups which can be used for building up the $\infty(BO_2)^{-1}$ chains of the lattice will be rather difficult. It could be done by a breaking up of the chain fragments existing in the melt into very small constituents, for example single radicals $(BO_2)^{-1}$ and an addition of these small groups to the lattice. However, this involves a breaking of the bonds within the chain fragments and, therefore, requires a great amount of energy. It could also be done by adding the chain fragments directly, but this will be a very slow process, owing to the length and the unsymmetrical form of the chains, which will make their translation through the muddle of other chains and their final orientation extremely difficult. The total result will be that the crystallization of the melt will proceed extremely slowly. The melt will show a strong tendency to get supercooled and when the temperature has fallen below a certain limit, the mobility of the ions, chain fragments and crystallites will be so small that a rigid glass is obtained.

Above, a special compound has been selected as an example of a glass forming substance, the crystals of which contain unlimited chain radicals, but it is the author's opinion that all glass forming substances containing such chains behave in a similar manner, and further that the glass forming tendency of large groups of mainly inorganic substances has similar causes.

The atoms of the metalloids often seem to have an especially marked tendency to coordinate oxygen atoms with strong bonds in quite a definite way. This characteristic coordination is then often found both in the oxides and the anions of the corresponding acids or salts. As an example the silicon atom will be chosen which is always situated in the center of a tetrahedron with oxygen atoms in its corners. Such SiO_4 tetrahedra, which may be considered as radicals $(SiO_4)^{-4}$, characterize the orthosilicates. If now the ratio Si : O of a Si-O compound is higher than 0.25 there will not be enough oxygen atoms for the formation of discrete SiO_4 tetrahedra. In this case the desired coordination can be attained if different tetrahedra have corners in common. Then, for example, groups $(Si_2O_7)^{-6}$ of two tetrahedra, or rings $(SiO_3)_n^{-2n}$ composed of a varying number of tetrahedra allow the desired coordination. At the proportion Si : O = 1 : 3 unlimited chains $\infty(SiO_3)^{-2}$ can also be formed, which characterize the pyroxene group. Similar chains, only with a more complicated structure and the composition $\infty(Si_4O_{11})^{-6}$ characterize the structure of the amphiboles. At the still higher Si : O ratio of 0.4, the number of oxygen atoms available for coordination around the silicon atoms is so low that radicals with an unlimited extension in two dimensions are formed. These sheet radicals have the composition $\infty(Si_2O_5)^{-2}$ and are found in the micas and the mica-like minerals. In silica, the ratio Si : O has reached the value 0.5 and here the SiO_4 tetrahedra must be linked together in a three-dimensional net. Corresponding silicates exist in which part of the silicon is replaced by aluminum. The excess in negative charge thus formed, is balanced by metallic cations, distributed in the interstices between the $(Si, Al)O_4$ tetrahedra. The framework of such tetrahedra can then be considered as a negative radical, unlimited in three dimensions. The minerals belonging to the felspar group have this structure.

In the silicates, containing small discrete radicals, or endless chain or sheet radicals, the forces within the radicals are certainly much stronger than the ionic forces between the different radicals and the cations. At the melting point these weak ionic bonds will lose their directional character, and the lattice will disintegrate but the radicals are still preserved to a certain degree. That is, the small closed radicals will probably maintain their structure while the unlimited radicals will break into fragments and get more or less deformed, but the linking together of the tetrahedra will probably be about the same in the fragments as in the original endless radicals. The tendency of these silicate melts to supercooling and glass formation will certainly depend very much on the size of these radicals or radical fragments and is likely to increase with increasing dimensions and irregularity of the latter.

The behavior of silica at the melting point must be somewhat different as Si-O bonds keep the whole three-dimensional structure together. The Si-O bonds are all equivalent at low tempera-

tures, but this is certainly not the case at the melting point, where the thermal motion of the atoms is very high. Consequently, the lattice will break up along lines of weakness, but it is to be assumed that the tendency of the silicon atoms to coordinate four oxygen atoms will still exist, thus causing three-dimensional groups of linked SiO_4 tetrahedra to remain in the melt. The principles governing the linkage of the tetrahedra within these groups are certainly about the same as in the silica modifications but the directional forces are so weak that the structure within these groups must be very irregular. Consequently, one cannot say that parts of the original lattice exist in the melt (as is expected by the "crystallite" theory). In this way a sort of irregular three-dimensional groups of SiO_4 tetrahedra linked together are formed, which will make the crystallization very difficult, because of the still existing strong Si-O bonds. The glass, formed when the cooling velocity is high enough, will be constituted in very much the same way as is assumed by Zachariasen, and the measurements of Warren,[3] which were considered to verify Zachariasen's theory, are also in accordance with the present view.

The felspars probably behave in the same way although one has here to consider the metallic cations which, at the melting point, are disengaged from their definite positions in the lattice.

One sees how the tendency of the silicon atoms always to attain a certain oxygen coordination causes large groups of atoms to appear in the melt. It must be observed that it is not necessary to regard these groups as remnants of similar groups, previously existing in a crystal. A chemical reaction can take place in a melt and give rise to a composition at which groups of some sort are formed in the melt. It is probable, however, that if a melt can be obtained by melting a crystal, both will contain groups within which the polyhedra are linked in essentially the same way. In discussing the glass forming tendency of a substance the knowledge of its crystal structure is, therefore, important.

From what has been said now it seems as if the glass forming properties of silicates and silica could be accounted for by the assumption that the large and irregular groups existing in the melt prevent the crystallization. The observations do not allow of a detailed discussion of the parallellism between structure and glass forming tendency of silicates, but it is well known that the orthosilicates seldom or never form glass, while silica and the felspar group, which contain three-dimensional nets, are extremely liable to glass formation. The glass forming tendency of the other silicates rank them between these two groups which are also the two extremes regarding the structure.

This experience from pure silicates shows that the tendency to crystallize decreases when the ratio Si : O increases. The same must be the case in the mixtures composing technical glass. Although technical glass does not correspond to definite crystal structures with the same composition as the glass in question, one can certainly assume that the type of Si-O groups, dominating in a glass, is determined by the ratio Si : O. Zachariasen has pointed out that this ratio in technical, boron free glass generally lies at about 0.40, and considers this as a proof that the Si-O groups are here three-dimensional. This may be the case, although sheets $n(Si_2O_5)^{-2}$ are also compatible with this ratio.

Summarizing the above it seems as if a melt contains atom groups which are kept together with strong (probably in many cases homopolar) forces, and if these groups are so large or irregular that their direct addition to the crystal lattice is difficult, such a melt will show a tendency to supercooling and glass formation. In melts of ionic crystals where the ions are formed by single atoms or small radicals this tendency must be very small. The same is the case in molecular structures with small molecules. The glass forming tendency then increases with increasing dimensions or irregularity of the radicals or molecules, and seems to be especially large when the corresponding crystals contain radicals or molecules, unlimited in one or more directions. Fragments of similar constitution will then occur in the melt and make the crystallization difficult.

It is interesting to note that, with the exception of the elements capable of glass formation, nearly all inorganic glasses consist of oxides of

[3] B. E. Warren, Z. Krist. **86**, 349 (1933).

metalloids or the acids and salts containing anions corresponding to these oxides. The glass forming tendency in these cases is probably to be seen in connection with the fact mentioned above that certain metalloid atoms tend to coordinate oxygen atoms in a definite way, and that a linking together of the corresponding polyhedra will occur if the number of available oxygen atoms is smaller than necessary for the formation of discrete groups with the required coordination.

From the literature it seems as if only the oxides B_2O_3, SiO_2, P_2O_3, P_2O_5, GeO_2, As_2O_3 and As_2O_5 are known in the vitreous state. The metalloids B, Si, P, Ge and As tend to coordinate 3 or 4 oxygen atoms and as is seen from the formulae such a coordination is impossible if some corners of the oxygen triangles or tetrahedra are not shared. Thereby groups of polyhedra are formed which make crystallization difficult. The structures of SiO_2 and GeO_2 confirm this assumption while the structures of the other oxides except As_2O_3 are unknown. The As_2O_3 structure can be interpreted as a molecular structure of cubic symmetry, composed of As_4O_6 molecules. This structure does not show the existence of any large or irregular groups, and one must assume that either the As_4O_6 molecules are large or irregular enough to delay the crystallization or that the melt contains other groups. It is not impossible that the monoclinic modification of As_2O_3 which is known as claudetite and which, according to Smits and Beljaars,[4] is stable above 221°C, has a structure of linked polyhedra and that the groups in the melts are connected with this structure. The fact that the density of the cubic modification (3.64) is lower than the density of the glass (3.68) while the density of the monoclinic modification is higher (4.00), also seems to indicate that the glass is related to the latter, although this cannot be considered as a definite proof (cf. later).

Reports of other oxides than the above-mentioned existing in the vitreous state are very unreliable. V_2O_5 solidifies as glass when mixed with P_2O_5 but several efforts made by the author to obtain pure V_2O_5 glass have been unsuccessful. One could perhaps expect the existence of vitreous SO_3 as the sulphur atoms undoubtedly have a strong tendency to coordinate four oxygen atoms. This can only be effected if the tetrahedra are linked together, forming unlimited chains or closed rings.

The question why BeO does not form glass is discussed by Zachariasen. This may depend on the structure of BeO, but according to what has been said above, the fact that the Be-O bond at least partially is of an ionic character,[5] may also be an explanation. On the other hand BeF_2 can form glass. The Be-F bonds are not ionic,[6] and the structure consists of a three-dimensional network of BeF_4-tetrahedra linked together.[7] The difference between the Be-O and the Be-F bonds is also shown by the fact that BeO has a mainly basic character, while BeF_2 has the character of an anhydrofluoric acid. The formation of beryllates is known, although they are very unstable, while stable fluoberyllates are easily obtained.

The glass forming oxides mentioned above, are all acid anhydrides, and this fact is certainly connected with the non-ionic character of their bonds. The tendency of attaining a certain oxygen coordination by means of linked polyhedra will also remain in the corresponding acids or salts. If the oxides combine with water or basic oxides, forming acids or salts, the number of oxygen atoms available for the formation of coordinated polyhedra will increase. If a melt of an oxide contains groups of polyhedra with a three-dimensional linkage, the addition of a basic oxide will make first a two-dimensional and then a one-dimensional linkage possible. A further addition of the basic oxide will cause the appearance of closed discrete radicals. Consequently, the glass forming ability of the melt will decrease when it is getting more basic. We have already seen this to be the case for the silicates. Other substance groups which behave in the same way are the borates and the phos-

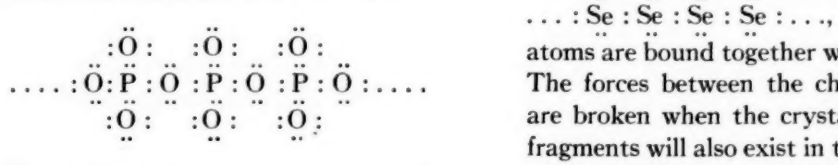
[4] A. Smits and E. Beljaars, Zeits. f. physik. Chemie **A167**, 273 (1933).

[5] L. Pauling, J. Am. Chem. Soc. **49**, 788 (1927); G. v. Hevesy, Zeits. f. physik. Chemie **127**, 407 (1927).

[6] B. Neumann and H. Richter (Zeits. f. Electrochemie **31**, 484 (1925)) report a very small electrical conductivity of molten BeF_2.

[7] E. Brandenberger, Schweiz. Min. Petr. Mitt. **12**, 243 (1932).

phates. It is well known that the melts of B_2O_3 with alkali oxides and the oxides of Tl and Ag form glass when the content of B_2O_3 is high and that they crystallize more easily when the B_2O_3 content decreases. The glass forming tendency is largest for B_2O_3 which even cannot be obtained in crystalline form,[8] is still very high for the tetraborates, $M_2B_4O_7$, and lower, but still often very marked for the metaborates, MBO_2. We know that orthophosphoric acid, H_3PO_4, has a marked tendency to supercool, and this seems to indicate that, although the oxygen content permits the formation of discrete $(PO_4)^{-3}$ radicals, not only electrostatic forces are at hand between the radicals in the melt. However, the glass forming tendency increases when the water is driven away from the orthophosphoric acid and first pyrophosphoric acid, $H_4P_2O_7$, and then metaphosphoric acid, HPO_3, is formed. Also the metaphosphates are extremely liable to glass formation. One has probably here chains



which are either open or forming closed rings $(PO_3)_n^{-n}$. The polymerization tendency of the metaphosphates is so high that it also persists in aqueous solutions.

The orthophosphoric acid, H_3PO_4, may serve as an example that a substance can possess a tendency to glass formation, although no causes seem to exist for the formation of large or irregular groups. However, it seems probable that the viscosity and the glass forming tendency of such a melt are caused by larger groups than $(PO_4)^{-3}$, formed by polymerization. The same may be the case with the recently investigated salt $K_2Mg(CO_3)_2$,[9] which is formed in a vitreous state by melting together K_2CO_3 and $MgCO_3$ at a CO_2 pressure of 1200 atm.

Turning over from the glasses, where the oxygen atoms evidently play a great role, to the glass-forming elements, we are not to await any glass formation for metals, as the atoms in a metallic melt are certainly not linked together by strong forces so as to form any large groups. Of the metalloids, only carbon, sulphur and selenium are known in states which seem more or less vitreous. The investigations of Arnfelt[10] make it probable that already the most amorphous forms of carbon contain C_6 rings linked together in sheets. The strong forces within these sheets make the crystallization (graphitization) of carbon a very slow process. One has to expect the existence of these sheets even in the mineral shungite, which has almost complete vitreous properties and almost could be characterized as a carbon glass.

In the trigonal form of selenium, unlimited chains of atoms exist, within which the distance between adjacent atoms is much smaller than between the chains. These chains are probably to be considered as unlimited molecules $\ldots : \ddot{\underset{\ddot{}}{\text{Se}}} : \ddot{\underset{\ddot{}}{\text{Se}}} : \ddot{\underset{\ddot{}}{\text{Se}}} : \ddot{\underset{\ddot{}}{\text{Se}}} : \ldots$, within which the atoms are bound together with homopolar forces. The forces between the chains are weaker and are broken when the crystals melt, while chain fragments will also exist in the melt, thus causing a large tendency to glass formation. Tellurium has the same crystal structure as selenium but is not known with certainty in the vitreous state. The more pronounced metallic properties of this element are perhaps the cause of this exception.*

The crystal structures of the sulphur modifications are not yet known but in analogy to selenium this element probably has a tendency to form chains $\ldots : \ddot{\underset{\ddot{}}{\text{S}}} : \ddot{\underset{\ddot{}}{\text{S}}} : \ddot{\underset{\ddot{}}{\text{S}}} : \ddot{\underset{\ddot{}}{\text{S}}} : \ldots$ Whether these chains form unlimited molecules or close to rings with a limited molecular weight (S_8?), the necessary causes for glass formation seem to exist.

A mentioning of the large groups of organic substances forming glass will close this discussion of different substances known in the vitreous

[8] N. W. Taylor and S. S. Cole (J. Am. Chem. Soc. **56**, 1648 (1934)) have recently reported that they have succeeded in obtaining crystalline B_2O_3.

[9] W. Eitel and W. Skaliks, Zeits. f. anorg. Chemie **183**, 263 (1929).

[10] H. Arnfelt, Arkiv f. Matematik, Astronomi och Fysik **B23**, No. 2 (1932), (in English); and later investigations not published yet.

* The observation made by Toepler (Ann. d. Physik **53**, 343 (1894)) that the volume of molten tellurium decreases considerably when the temperature is raised above the melting point might perhaps indicate a break down of the tellurium chains.

state. Here the melts will in most cases contain either large and irregular molecules or polymerized groups of molecules linked together with rather strong forces and the retarding of the crystallization will be easily understood.

The general properties of the glasses seem to be explicable at least qualitatively by the theory discussed above. The glass forming melt must possess a rather high viscosity owing to the large and irregular groups existing in it, but this as well as many other properties of the melt ought to be dependent on the foregoing treatment. The size of the groups certainly varies with the temperature and as equilibrium probably will be established very slowly in such a viscous medium, the properties of a melt even at a given temperature must depend on the heat treatment preceding the measurements. The same will be the case for the solidified glass. Such hysteresial effects are often shown by the measurements.

The isotropy of the glasses is explained by the irregular distribution of the molecules or atomic groups forming the glass. These circumstances also prevent all gliding and thus contribute to the hardness and brittleness which characterize most glasses.

From the constitution of the glasses it is quite clear that their energy must be slightly higher than the energy of the corresponding crystals. The numerous puzzling features of the curves of the heat capacities of glasses can, however, not be explained in detail. These features are moreover often caused by individual properties of the glass, which probably have nothing to do with the vitreous state in general.

The specific volume of a glass is in most cases higher than that of the corresponding crystals. This follows from the fact that the crystals of glass forming substances generally melt under expansion, and that the specific volume curve of the glass must be a continuation of that of the liquid. However, the volume curves of glasses often show irregularities and in some cases these are so large that at low temperatures the specific volume of the glass is lower than that of the crystals. For example, it was shown already by Tammann[11] for $Sr(BO_2)_2$, which melts at 1100°C under expansion, that the coefficient of thermal expansion of the glass is so much higher than that of the crystals, that the specific volume curves cut at $420° \pm 100°$.

Electrical conductivity at high temperatures is no general feature of the vitreous state. The conductivity is certainly mainly electrolytic and, therefore, will reach high values only if the glass contains ions, while for example glasses of pure oxides show rather low conductivities. According to the above it is always the anions of the glass which form the groups causing the viscosity and the slow crystallization of the glasses, and consequently, the conductivity must be due nearly entirely to the cations.

Summary

If a melt contains atom groups, which are kept together with strong (probably in many cases homopolar) forces and if these groups are so large or irregular that their direct addition to the crystal lattice is difficult, such a melt will show a tendency to supercooling and glass formation. In melts of ionic crystals where the ions are formed by single atoms or small radicals and no polymerization occurs, this tendency must be very small. The same is the case in molecular structures with small molecules and in metallic melts. The glass forming tendency then increases with increasing dimensions or irregularity of the radicals, molecules or polymerized groups, and seems to be specially large when the corresponding crystals contain radicals or molecules, unlimited in one or more dimensions. This is probably the case with nearly all inorganic glasses, and the same forces as those which cause the existence of these unlimited groups in the crystals will probably cause the formation in the melt of rather large and irregular groups of a similar constitution, making the crystallization difficult.

In the large group of inorganic glasses consisting of oxides of metalloids, and the acids and salts, containing anions corresponding to these oxides, the formation of unlimited groups is caused by the strong tendency of these metalloids to coordinate oxygen in a definite way. If the number of available oxygen atoms is smaller than necessary for the formation of dis-

[11] G. Tammann, *Kristallisieren und Schmelzen*, p. 49. Leipzig, 1903.

crete polyhedral groups with the required coordination, the polyhedra will be linked together sharing oxygen atoms. The oxygen content will determine the constitution of the groups formed by this linking together of the polyhedra and, consequently, the tendency to glass formation. In accordance with this, the glass forming tendency in the systems of SiO_2, B_2O_3 and P_2O_5 with basic oxides decreases with increasing content of basic oxide.

Finally, the author wants to thank Mr. H. Arnfelt of this Institute for many valuable discussions, which have contributed to the growth of the ideas appearing in this paper.

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Addition of Symmetrical Diatomic Molecules to Benzene

ALBERT SHERMAN,* C. E. SUN AND HENRY EYRING, *Frick Chemical Laboratory, Princeton University*

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The reaction of hydrogen and benzene to form 1,2-dihydrobenzene is considered, and the activation energy of the reaction is calculated with various assumptions concerning directed valence. It is shown that one may calculate approximate heats of reactions by considering exchange integrals only between electrons on neighboring atoms in a molecule, but this is not possible in calculating activation energies. The hydrogenation of benzene is considered as an eight electron problem, and the system serves to illustrate the degree of simplification of the secular equation arising from the symmetry of the system. The matrix elements of the factored equation are calculated. Activation energies of the reactions involved in the adsorption of H_2 and C_6H_6 on Ni have been calculated and lead one to expect that the reaction might be achieved more easily catalytically.

INTRODUCTION

THE addition of a diatomic molecule to benzene is particularly interesting in that it involves a rearrangement of the six electrons in benzene which before reaction resonate chiefly between the two possible ways of drawing three double bonds (i.e., the two Kekulé structures). After the addition reaction there are two conjugate double bonds.

Various aspects of the problem relating to benzene molecules have been discussed by Hückel,[1] Penney,[2] Pauling and Wheland,[3] Seitz and Sherman,[4] to mention only a few. However, the carrying through of an approximate calculation of the activation energy for a reaction of the type $H_2+C_6H_6\rightarrow C_6H_8$ has not been previously undertaken.

CALCULATION

a. Quantum mechanical considerations

In a reaction of the type $H_2+C_6H_6\rightarrow C_6H_8$ we consider eight electrons, one on each atom of the diatomic molecule and the six in benzene which do not form unique bonds. The secular equation for eight electrons is of fourteenth degree, and we could, of course, use the fourteenth degree secular equation of Eyring and Kimball,[5] in this case. But in the system we are considering, shown in Fig. 1, there is a plane of symmetry

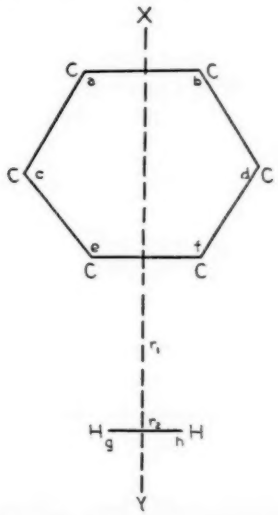


FIG. 1. Addition of H_2 to benzene to form 1,2-dihydrobenzene.

* National Research Council Fellow in Chemistry, at the University of Wisconsin, 1933–34.

[1] Hückel, Zeits. f. Physik **70**, 204 (1931).

[2] Penney, Proc. Roy. Soc. **A146** (1934).

[3] Pauling and Wheland, J. Chem. Phys. **1**, 362 (1933).

[4] Seitz and Sherman, J. Chem. Phys. **2**, 11 (1934).

[5] Eyring and Kimball, J. Chem. Phys. **1**, 239 (1933).

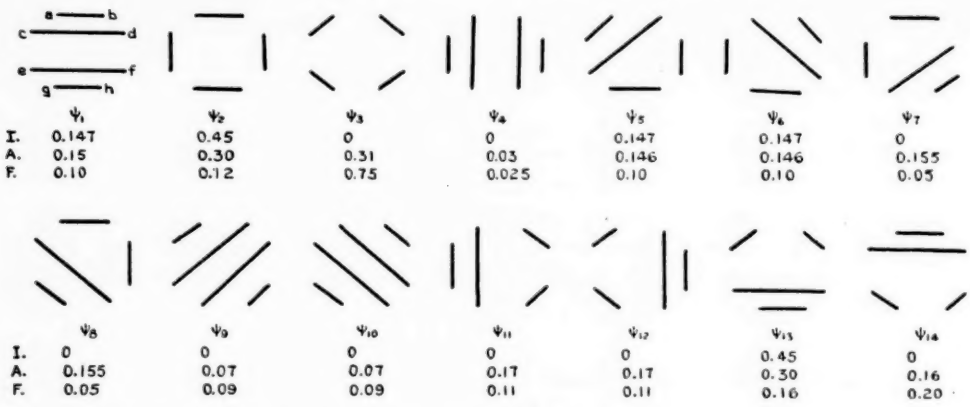


FIG. 2. The 14 linearly independent bond wave functions for 8 electrons with their coefficients in the wave function representing the initial activated and final state of the system H_2 and C_6H_6 for the reaction $H_2+C_6H_6 \rightarrow$ 1,2-dihydrobenzene.

xy,—i.e., if the system is rotated through 180° about the line xy the resulting system is physically identical with the original system. The rotation corresponds to sending a into b, b into a, c into d, d into c, etc. As we shall see, this symmetry enables us to factor our secular equation into a product of a tenth and a fourth degree equation.

The role which the symmetry of a system plays in factoring the secular equation has been formally discussed by Eyring, Frost and Turkevitch[6] and by Seitz and Sherman.[7] We therefore merely define wave functions which do factor the fourteenth degree equation, and calculate the corresponding matrix elements.

It was mentioned above that in general the secular equation for eight electrons is of fourteenth degree. This means that we express the wave function for the system as a linear combination of fourteen independent wave functions, i.e.,

$$\psi = \sum_{K=1}^{14} S_K \psi_K. \qquad (1)$$

The fourteen functions $\psi_1, \psi_2, \cdots \psi_{14}$, that are used are the so-called bond wave functions.[8] A convenient independent set is represented below in Fig. 2.

The diagram of the wave function ψ_1 indicates the position of the atoms for the other wave functions also. For any configuration of the atoms the actual wave function for the system H_2+benzene is some linear combination of the independent set of fourteen. The coefficients which multiply the wave functions for the initial state (with the H_2 molecule remote from the benzene), the final state of dihydrobenzene, and the intermediate activated state are indicated in the appropriate rows beneath each wave function.

It is perhaps well to point out that it is meaningless in the chemical sense to speak of the system having at a particular moment a particular pure bond state. This is because no chemical experiment can be designed which would show the system to oscillate between the fourteen ways of drawing the bonds, since the passage from one bond structure to another involves motion of electrons which, because of their small mass, pass through all the bond states during a time interval in which atomic nuclei (the test bodies of chemistry) do not move appreciably. Thus the potential energy of an atomic system depends only on the averaged position of the electrons, and this is given by the linear combination of the fourteen bond wave functions appropriate to the particular atomic configuration.

The manner in which atoms are bonded is in a certain sense a much less fundamental chemical concept than the energy of the corresponding

[6] Eyring, Frost and Turkevitch, J. Chem. Phys. **1**, 777 (1933).
[7] Seitz and Sherman, J. Chem. Phys. **2**, 11 (1934).
[8] Sherman and Eyring, J. Am. Chem. Soc. **54**, 2661 (1932). Eyring and Kimball, J. Chem. Phys. **1**, 239 (1933).

configuration. It is, for example, the energy which enters into the thermodynamic and rate equations describing the behavior of chemical systems. In fact, the interest in the manner of binding is about proportional to the extent to which it summarizes energy relations. It is this same fact which makes energy surfaces so fundamentally interesting.

Suppose, now, instead of using the fourteen wave functions given in Fig. 2 we define a new set of fourteen as follows:

$$\begin{array}{lll} \phi_1=\psi_1, & \phi_6=\psi_7+\psi_8, & \phi_{11}=\psi_5-\psi_6, \\ \phi_2=\psi_2, & \phi_7=\psi_9+\psi_{10}, & \phi_{12}=\psi_7-\psi_8, \\ \phi_3=\psi_3, & \phi_8=\psi_{11}+\psi_{12}, & \phi_{13}=\psi_9-\psi_{10}, \\ \phi_4=\psi_4, & \phi_9=\psi_{13}, & \phi_{14}=\psi_{11}-\psi_{12}. \\ \phi_5=\psi_5+\psi_6, & \phi_{10}=\psi_{14}, & \end{array}$$

This set of fourteen wave functions possesses the property of falling into two non-combining sets of ten and four, i.e., the matrix element

$$\int \phi_i H \phi_j d\tau = 0$$

if $i=1, 2, 3, \cdots 10$ and $j=11, 12, 13,$ or 14.

This of course means that the fourteenth degree secular equation factors into a product of a tenth and fourth degree equation, so that for any system of eight electrons possessing the symmetry of Fig. 1 we need only solve a tenth degree equation. In the calculation of activation energies we are interested in finding the lowest of the fourteen roots and since this lies in the tenth degree equation, we need only be concerned with it.

The wave functions $\phi_1, \phi_2, \cdots \phi_{10}$ do not form an orthogonal set ($\int \phi_i \phi_j d\tau \neq 0$ when $i \neq j$), but a new set, formed from a linear combination of the ϕ's, may be found which are orthogonal,—and, hence more tractable. These are defined below in Table I and the matrix components between them given in Table II.

TABLE I.

$$\begin{aligned} \chi_1&=\phi_1 \\ \chi_2&=\phi_2-1/2\phi_1 \\ \chi_3&=\phi_3-1/2\phi_1 \\ \chi_4&=\phi_4-\phi_3-\phi_2+1/2\phi_1 \\ \chi_5&=\phi_5-1/2\phi_1 \\ \chi_6&=\phi_6-\phi_5-\phi_2+1/2\phi_1 \\ \chi_7&=\phi_7-1/2\phi_8-1/2\phi_3+1/4\phi_1 \\ \chi_8&=\phi_8-\phi_7-1/2\phi_6+1/2\phi_5-1/2\phi_4+1/2\phi_3+1/2\phi_2-1/4\phi_1 \\ \chi_9&=\phi_9+3/5\phi_8-8/5\phi_7-4/5\phi_6+4/5\phi_5-4/5\phi_4 \\ &\qquad +4/5\phi_3+4/5\phi_2-2/5\phi_1 \\ \chi_{10}&=\phi_{10}-3/4\phi_9-1/4\phi_8+2/3\phi_7+1/2\phi_6-1/3\phi_5 \\ &\qquad +1/2\phi_4-1/3\phi_3-\phi_2+1/6\phi_1 \end{aligned}$$

b. Activation energies

The tenth order secular equation given in Part *a* was used to calculate the activation energies of several reactions involving the configurations of eight electrons. This was done in the usual way by constructing a potential energy surface.[9] The various exchange and coulombic integrals were evaluated as usual, by constructing morse potential energy curves for the various bonds involved.

Let us now consider the reaction $C_6H_6+H_2 \rightarrow C_6H_8$ in some detail. The calculations correspond to the approach of H_2 to benzene in a plane making such an angle with the plane of the benzene ring as corresponds to that existing in 1,2-dihydrobenzene. At the beginning of the reaction the distance r_1 of Fig. 1 is very large and r_2 has the value for the normal distance between hydrogen atoms in H_2. As the reaction proceeds r_1 decreases and r_2 increases. If the various integrals involved are evaluated from Morse potential energy curves, which involves the assumption that the value of these integrals is a function only of the distance between atoms, a potential energy surface results which gives an activation energy for the reaction of 95.6 kg cal. and a value for the heat of the reaction, $\Delta H=+85.1$ kg cal., i.e. 1,2-dihydrobenzene is 85.1 kg cal. less stable than H_2+benzene. Thermochemical data indicate that 1,2-dihydrobenzene is slightly more stable than H_2+benzene.

Now Pauling and Wheland [10] and Pauling and Sherman[11] have calculated heats of reaction,—or, rather, resonance energies—of a large number of organic molecules, and assumed the exchange integral between all pairs of electrons other than those on neighboring atoms is zero, and obtained quite satisfactory results, as judged by numerical agreement. Their assumption is equivalent to saying that the wave functions of electrons on atoms in polyatomic molecules do not possess the spatial symmetry existing in atoms forming

[9] Eyring and Polanyi, Zeits. f. physik. Chemie **B12**, 279 (1931); Eyring, J. Am. Chem. Soc. **53**, 2537 (1931); Sherman and Eyring, ibid. **54**, 2661 (1932); Kimball and Eyring, ibid. **54**, 3876 (1932); Eyring, Sherman and Kimball, J. Chem. Phys. **1**, 586 (1933).

[10] Pauling and Wheland, J. Chem. Phys. **1**, 362 (1933).

[11] Pauling and Sherman, ibid. **1**, 606 (1933).

TABLE II.

	$H_{1,1}$	$H_{1,2}$	$H_{1,3}$	$H_{1,4}$	$H_{1,5}$	$H_{1,6}$	$H_{1,7}$	$H_{1,8}$	$H_{1,9}$	$H_{1,10}$	$H_{2,2}$	$H_{2,3}$	$H_{2,4}$
C	1	0	0	0	0	0	0	0	0	0	3/4	0	0
ab	0	3/2	3/2	0	0	0	0	3/4	6/5	0	0	0	3/4
ad	−3	−3/2	−3/2	−3/2	0	0	0	−3/4	−6/5	0	−3/4	−3/4	−3/4
af	0	0	0	3/2	0	0	0	0	0	0	−3/2	3/4	0
ag	−1	0	0	0	3/2	0	0	0	0	0	−3/4	0	0
ah	−1	0	0	0	0	−3/2	0	0	0	0	−3/4	0	0
cg	−1	0	0	0	0	0	0	3/4	6/5	0	−3/4	0	0
ch	−1	0	0	0	−3/2	0	0	0	0	0	−3/4	0	0
eg	−1	0	0	0	0	3/2	0	0	0	0	−3/4	0	0
eh	−1	0	0	0	0	0	0	−3/4	−6/5	0	−3/4	0	0
gh	1	0	0	0	0	0	0	0	0	0	3/4	0	0

	$H_{2,5}$	$H_{2,6}$	$H_{2,7}$	$H_{2,8}$	$H_{2,9}$	$H_{2,10}$	$H_{3,3}$	$H_{3,4}$	$H_{3,5}$	$H_{3,6}$	$H_{3,7}$	$H_{3,8}$	$H_{3,9}$
C	0	0	0	0	0	0	3/4	0	0	0	0	0	0
ab	3/4	−3/4	−3/8	3/8	0	−1/4	0	3/4	0	0	0	0	−27/20
ad	−3/2	3/2	3/4	−3/4	−3/5	1/2	−3/4	−3/4	0	0	0	0	21/10
af	3/4	−3/4	−3/8	3/8	3/5	−1/4	−3/2	0	0	0	0	0	0
ag	−3/4	3/2	3/8	−3/8	−3/5	1/4	−3/4	0	0	0	9/8	0	0
ah	0	−3/4	−3/8	3/8	3/5	−1/4	−3/4	0	0	0	0	−3/8	−3/5
cg	0	0	3/8	−3/4	−3/10	5/8	−3/4	0	0	3/4	0	0	−27/20
ch	3/4	−3/2	−3/8	3/8	3/5	−1/4	−3/4	0	0	0	−9/8	0	0
eg	0	3/4	3/8	−3/8	−3/5	1/4	−3/4	0	0	0	0	3/8	3/5
eh	0	0	−3/8	3/4	3/10	−5/8	−3/4	0	0	−3/4	0	0	3/5
gh	0	0	0	0	0	0	3/4	0	0	0	0	0	0

	$H_{3,10}$	$H_{4,4}$	$H_{4,5}$	$H_{4,6}$	$H_{4,7}$	$H_{4,8}$	$H_{4,9}$	$H_{4,10}$	$H_{5,5}$	$H_{5,6}$	$H_{5,7}$	$H_{5,8}$	$H_{5,9}$
C	0	3/4	0	0	0	0	0	0	3/4	0	0	0	0
ab	9/16	−3	−3/4	3/4	−3/8	3/8	27/20	−13/16	−3/2	0	7/8	−3/8	−6/5
ad	−9/8	−3/4	3/2	−3/2	3/4	−3/4	−21/10	13/8	−9/4	3/4	−7/8	−9/8	−6/5
af	0	3/2	−3/4	3/4	3/8	−3/8	−6/5	1/4	0	−3/4	0	3/2	12/5
ag	0	−3/4	3/4	−3/4	−3/8	3/4	9/5	−1/4	3/4	3/4	0	−3/8	−3/5
ah	0	−3/4	−3/4	3/4	0	−9/8	−3/10	−3/8	−3/4	−3/4	0	3/8	3/5
cg	9/16	−3/4	3/4	0	−3/4	3/4	15/4	−17/16	−3/4	0	0	0	−3/5
ch	0	−3/4	−3/4	3/4	3/8	−3/4	−9/5	1/4	3/4	−3/4	0	3/8	3/5
eg	0	−3/4	3/4	−3/4	0	9/8	3/10	3/8	−3/4	3/4	0	−3/8	−3/5
eh	0	−3/4	−3/4	0	0	0	−9/5	0	−3/4	0	0	0	3/5
gh	0	3/4	0	0	0	0	0	0	−3/4	0	0	0	0

	$H_{5,10}$	$H_{6,6}$	$H_{6,7}$	$H_{6,8}$	$H_{6,9}$	$H_{6,10}$	$H_{7,7}$	$H_{7,8}$	$H_{7,9}$	$H_{7,10}$	$H_{8,8}$	$H_{8,9}$	$H_{8,10}$
C	0	3/4	0	0	0	0	9/16	0	0	0	15/16	0	0
ab	0	3/2	−3/8	3/4	9/5	−1/4	−9/8	3/16	111/40	−33/32	−21/4	−201/40	21/8
ad	3/2	−27/4	−9/8	3/4	18/5	−21/8	−9/16	−3/8	−3/4	9/16	9/8	33/10	−21/16
af	−3/2	0	3/2	−3/2	−27/5	23/8	−9/8	−3/16	−3	9/8	3/16	33/10	−17/8
ag	0	−9/4	−3/8	2	22/5	−1/4	9/16	3/16	3/5	0	−2	−16/5	5/8
ah	−3/4	9/4	3/8	−2	−22/5	1	−9/16	3/4	−3/10	3/8	5/4	11/4	−5/8
cg	0	3/4	0	5/8	13/10	0	−9/16	−3/8	63/40	−27/32	−19/16	−61/40	9/8
ch	0	3/4	3/8	−2	−22/5	1/4	9/16	−3/16	−3/5	0	13/8	13/5	−5/8
eg	3/4	−3/4	−3/8	2	22/5	−1	−9/16	3/4	−3/10	−3/8	−19/8	−61/20	5/8
eh	0	−3/4	0	−5/8	−13/10	0	−9/16	−3/4	0	0	1/16	17/20	−5/16
gh	0	−3/4	0	0	0	0	−9/16	0	0	0	−15/16	0	0

	$H_{9,9}$	$H_{9,10}$	$H_{10,10}$	$H_{11,11}$	$H_{11,12}$	$H_{11,13}$	$H_{11,14}$	$H_{12,12}$	$H_{12,13}$	$H_{12,14}$	$H_{13,13}$	$H_{13,14}$	$H_{14,14}$
C	3/5	0	5/16	3/2	0	0	0	3/2	0	0	3/4	0	3/4
ab	−216/25	47/10	−101/32	−3	0	0	0	−3/2	3/4	3/4	−9/4	−3/2	−3/4
ad	117/25	−13/5	5/8	0	0	0	0	−3	−3/2	0	−3/2	0	−9/4
af	102/25	−73/20	7/4	−3/2	0	0	0	−3	3/4	−3/4	0	3/2	−3/4
ag	−128/25	1	−11/8	−3/2	0	3/4	−3/4	0	0	0	0	0	0
ah	41/10	−13/8	35/32	−3/2	0	−3/4	−3/4	0	0	0	−3/4	−3/4	0
cg	−167/50	107/40	−5/4	−3/2	−3/2	0	0	−3/2	0	0	0	0	0
ch	104/25	−1	1/8	−3/2	0	−3/4	3/4	0	0	0	−3/4	3/4	−3/4
eg	−259/50	3/8	−5/32	−3/2	0	3/4	3/4	0	0	0	0	0	−3/4
eh	53/50	1/8	5/32	−3/2	3/2	0	0	−3/2	0	0	0	0	0
gh	−3/5	0	−5/16	3/2	0	0	0	−3/2	0	0	−3/4	0	−3/4

diatomic molecules,—assumed by us in the above calculation. In other words, the value of the exchange integral between electron pairs in polyatomic molecules is not simply a function of the distance between atoms but also of *direction*, i.e., directed valence is considered.

If we consider exchange integrals between electrons on non-neighboring atoms to be zero the value of ΔH drops to +26.1 kg cal.,—in much better agreement with experiment. The fact that ΔH is still positive is primarily due to the incorrect (too small) C−H bond energy used in the calculation (see below).

It is to be emphasized that, although it has just been shown that it is much better to consider interactions between electrons on neighboring atoms only, for the initial and final state of the system, it is absolutely unsatisfactory to do so for the *whole* potential energy surface. Thus, if we consider interactions between electrons on neighboring atoms only, the calculated activation energy for the hydrogenation of

benzene to form 1,2-dihydrobenzene drops from 95.6 kg cal. to 36.6 kg cal. This is obviously too low (if a stronger C−H bond energy were used it would be even lower), as is realized when one recalls that the activation energy for the hydrogenation of C_2H_4, a more readily achieved reaction, is 43.3 kg cal. Also, the hydrogenation of benzene is carried out at catalytic surfaces at temperatures as high as 500–550°K, which means that in this temperature range the gas-phase reaction must still be relatively slow, corresponding to an activation energy greater than 40 kg cal.

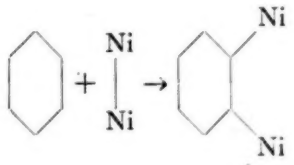
Another assumption that might be made—more reasonably perhaps, than to consider only interactions between electrons on neighboring atoms—is to set all non-neighboring interactions equal to zero except *eh* and *fg*. This gives an activation energy of 84.5 kg cal. If one neglected the electrons *a*, *b*, *c*, and *d* altogether, this being equivalent to considering the reaction as a four electron problem, the reaction would then be essentially the same as $C_2H_4+H_2\rightarrow C_2H_6$. All the experimental evidence, however, points to the latter reaction as being more easily achieved. Also, the heats of two reactions differ considerably.

The fact that directed valence is operative in polyatomic molecules probably accounts for the fact that the discrepancy between the calculated and experimental value for the activation energy is almost always such that the difference between calculated and experimental value is almost always positive, but the fact that this difference is small indicates the method used so far is approximately correct.

From what has been said above, it follows that the best semi-empirical method of calculating a potential energy surface for the reaction $C_6H_6+H_2\rightarrow C_6H_8$ is to do so by considering non-neighboring exchange integrals zero except *eh* and *fg*. This was done, by using a C−H bond strength of 120 kg cal., and a heat of reaction $\Delta H=-11$ kg cal. We consider these values to be the most reliable.[11a]

[11a] The value of 120 kg cal. for a C−H bond is for the diatomic molecule. The much lower observed values in compounds is a consequence of the repulsive interaction with the other groups attached to the carbon.

The activation energy of the reaction



was calculated in a manner similar to the one just described for the addition of H_2 to benzene, except that the percentage of coulombic binding in Ni−C was taken to be 22,—in qualitative accord with the known result that this percentage increases for metallic bonds.[12] With this assumption the calculated activation energy is found to be 3 kg cal., and $\Delta H=-5$ kg cal.

The activation energy of the reaction $H_2+Ni_2\rightarrow 2$ Ni−H was calculated in the usual manner, assuming the reaction involves the configuration of four electrons, one on each of the four atoms. The percentage of coulombic binding in Ni−H was taken as 20, and in Ni−Ni as 30. The activation energy was found to be 24 kg cal., and $\Delta H=-4.6$ kg cal.

Results

The results of all the calculations are summarized in Table III.

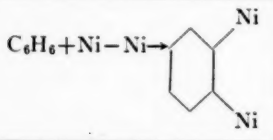
Discussion

The experimental data concerning the rate of the homogeneous gas-phase addition of H_2 to benzene are extremely meager and indirect. One cannot deduce a numerical value for the activation energy from the numerical data. As already mentioned, about all one can say is that it is high,—greater than 40 kg cal. The calculated value, therefore, is of the right order of magnitude. It shows that the homogeneous gas-phase addition of H_2 to benzene is impractical because, at the high temperature necessary to cause the reaction to have an appreciable rate, equilibrium would be against it.

From Table III it is seen that the calculated value of the activation energy is very much less sensitive to the various assumptions made than

[12] Bartlett and Furry, Phys. Rev. **37**, 1712 (1931), for example, show this percentage is 22 for Li_2, and Rosen, Phys. Rev. **38**, 255 (1931), calculates it to be 28.3 in Na_2.

TABLE III.

Reaction	Bond	Constants r_0 A	Constants ω_0 cm^{-1}	Constants D kg cal.	Assumptions (see Fig. 1)	ΔH kg cal.	A kg cal.
$C_6H_6+H_2\rightarrow C_6H_8$	H−H C−H	0.74 1.12	4375 2930	102.4 92.3	a. All integrals evaluated from Morse P.E. curves. Coulombic energy = 14%.	+85.1	95.6
					b. Exchange integrals between all electron-pairs = 0 except *ab*, *bd*, *df*, *ef*, *ce*, *ac*, *eg*, *fh*, and *gh*. These are determined as in *a*.	+26.1	36.6
					c. Same as *b* except *eh* and $fg \neq 0$.		84.5
	H−H C−H	0.74 1.12	4375 2930	102.4 120.0	Same as *c* above.	−11	78.3
	Ni−C Ni−Ni	1.92 2.38		60 20	Same as *c* above, except that for the Ni−C bond the coulombic energy was taken as 22% of bond energy, and for Ni−Ni bond as 30%.	−5	3
$H_2+Ni_2\rightarrow 2Ni-H$	Ni−Ni Ni−H	2.38 1.56		20 66.2	This reaction involves the configuration of 4 electrons, and was considered in the usual way.	−4.6	24

is the heat of the reaction. Thus, while the activation energy changes from 95.6 to 78.3 kg cal. the heat of the reaction changes from +85.1 to −11 kg cal. Thus, although there is frequently considerable uncertainty in bond strengths, the corresponding error in the activation energy is considerably less.

It is interesting to calculate the coefficients of Eq. (1) for the system C_6H_6 and H_2, using the wave functions of Fig. 2, for the initial, activated, and final states of the reaction $C_6H_6+H_2\rightarrow C_6H_8$. The results are given in Fig. 2, in the rows below the wave functions.

The value of the coefficients shows that the chemical reaction may be thought of as passing from an initial state where there is a fairly definite way of drawing the valence bonds (the Kekulé structures for benzene), through an activated state where one cannot represent the system even approximately by any particular way of drawing the bonds, to a final state where one can represent the system to a good approximation by a unique way of drawing the bonds. Thus, in the initial state the system may be represented approximately by $\psi = s_2(\psi_2+\psi_{13})$, and in the final state by $\psi = s_3\psi_3$, but at the activated state one must include at least ψ_1, ψ_2, ψ_3, ψ_5, ψ_6, ψ_7, ψ_8, ψ_{11}, ψ_{12}, ψ_{13} and ψ_{14}.

It is interesting to compare the calculated activation energy values for the hydrogenation of ethylene, butadiene, and benzene. The activation energy rapidly increases in going from C_2H_4 to C_6H_6, as, perhaps, would be expected. The hydrogenation of 1,2-dihydrobenzene would be closely analogous to that of butadiene, and of cyclohexane to that of ethylene, so that if benzene could be hydrogenated homogeneously one would expect the product to be cyclohexane and not 1,2-dihydrobenzene because the third molecule of H_2 would, at a given temperature,

TABLE IV.

Reaction	Activation energy (calc.)
$H_2+C_2H_4\rightarrow C_2H_6$	43.5[13]
$H_2+CH_2=CH-CH=CH_2$ $\rightarrow CH_3-CH=CH-CH_3$	65.0[14]
$H_2+C_6H_6\rightarrow C_6H_8$	78.5

[13] Sherman and Eyring, J. Am. Chem. Soc. **54**, 2661 (1932). The value given in this paper is based on 10 percent coulombic energy, and that given above is based on 14 percent coulombic energy.

[14] Eyring, Sherman and Kimball, J. Chem. Phys. **1**, 586 (1933).

enter the benzene nucleus more rapidly than the second molecule of H_2, which in turn would enter more rapidly than the first molecule. If this same relative order of activation energies held for the surface reactions one would also expect cyclohexane to be the product obtained upon catalytically hydrogenating benzene. This is apparently the case, although the surface reaction mechanism may be such that the separate steps are indistinguishable.[15]

The activation energies calculated for the reactions involving Ni are probably not very precise, but it is undoubtedly of significance that they are all of a lower order of magnitude than that for the hydrogenation of benzene. Thus, one might expect that, at least insofar as the rates of adsorption and desorption of H_2 and benzene on it are rate-determining, the hydrogenation of benzene could be achieved more easily on a catalytic nickel surface. This is experimentally the case, as was shown by Sabatier[16] and studied in detail by Dougherty and Taylor.[17] The latter authors found the catalytic reaction to be rapid from 60°C to 200°C.

[15] For example, see Ballandin, Zeits. f. physik. Chemie **B2**, 289 (1929).

[16] Sabatier, Ind. Eng. Chem. **18**, 1006 (1926).
[17] Dougherty and Taylor, J. Phys. Chem. **27**, 533 (1923).

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The Dipole Moments of Certain Monosubstituted Benzenes in the Vapor State

K. B. McAlpine and C. P. Smyth, *Frick Chemical Laboratory, Princeton University*
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The dielectric constants of the vapors of three monosubstituted benzenes have been determined over a range of temperature and used to calculate dipole moments as follows: fluorobenzene, 1.57×10^{-18}; chlorobenzene, 1.70×10^{-18}; nitrobenzene, 4.19×10^{-18}. These values are considerably higher than those found from previous measurements in solution and agree well with values calculated for the vapor state by the application of an empirical equation developed by Müller to measurements in solution.

THESE measurements were made nearly two years ago in an attempt to obtain reliable values for the moments of certain common dipoles which are frequently used in studies of molecular structure. They have taken on added interest because of recent work upon the dependence of the apparent value of a moment measured in solution upon the dielectric constant of the solvent.

The dielectric constants were measured with the apparatus previously described.[1] For fluorobenzene and chlorobenzene, the polarization P was calculated from the dielectric constant ϵ and the molar volume V as $P=[(\epsilon-1)/(\epsilon+2)]V$, the polarization-pressure curve at each absolute temperature T being extrapolated to zero pressure to obtain a value P_0 for use in the Debye equation, $P=a+b/T$. The value of the atomic polarization was calculated as $P_A=a-P_E$, the difference between a, the total induced polarization, and P_E, the molar refraction extrapolated to infinite wavelength. The dipole moments were calculated from the values of b as $\mu=0.01273\times10^{-18}(b^{1/2})$ and should be in error by no more than 0.01×10^{-18}.

The same procedure in the case of nitrobenzene, which had to be measured at lower pressures than the other two substances gave a value 4.03×10^{-18} and the abnormally large value 20.5 for the atomic polarization. When the moment was calculated at each temperature by subtracting P_E from the total polarization at zero pressure, values were obtained which rose from 4.20 to 4.25×10^{-18} with rising temperature. As it appeared probable that greater errors arose from extrapolating to zero pressure the polarizations at pressures below 200 mm than from deviations from the gas laws, the polarizations

[1] McAlpine and Smyth, J. Am. Chem. Soc. **55**, 453 (1933); J. Chem. Phys. **2**, 499 (1934).

for nitrobenzene were taken as the averages of from four to nine values at each temperature. These average values are listed under P_0 in Table I since they must differ by an almost negligible amount from the values at zero pressure. The probable error in the moment obtained for nitrobenzene is about 0.05×10^{-18}. The P_0 values are used to obtain the values of a and b in Table II.

TABLE I. *Polarizations.*

Fluorobenzene		Chlorobenzene		Nitrobenzene	
T, °K	P_0	T, °K	P_0	T, °K	P_0
343.6	69.9	373.6	79.6	442.1	282.6
371.4	66.8	403.7	75.7	442.3	281.7
414.1	62.5	429.8	73.1	483.0	262.0
453.2	59.3	476.1	69.0	504.2	251.2
507.0	55.8	518.4	66.2	539.1	239.3
				548.7	234.0

TABLE II. *Values of calculated constants.*

	a	P_E	P_A	b	$\mu\times10^{18}$
C_6H_5F	25.8	24.8	1.0	15190	1.57
C_6H_5Cl	31.7	29.9	1.8	17830	1.70
$C_6H_5NO_2$	37.7	31.6	6	108100	4.19

PURIFICATION OF MATERIALS

Fluorobenzene

Material from the Eastman Kodak Company was dried over calcium chloride and fractionated: b.p., 84.1° (750 mm); n_D^{20}, 1.46593.

Chlorobenzene

Material from the Eastman Kodak Company was shaken with concentrated sulfuric acid until the acid layer no longer became colored. It was then washed with water, with dilute potassium bicarbonate solution, and again with water, was dried over calcium chloride and distilled; b.p., 131.1°; n_D^{20}, 1.52459. A thorough drying of the material over phosphorus pentoxide and subsequent distillation gave a product with the same refractive index and a boiling point of 130.7° at 755 mm.

Nitrobenzene

Merck's material was crystallized five times from its own melt, dried over phosphorus pentoxide, and distilled under reduced pressure; freezing point, 5.71–5.53°; n_D^{20}, 1.55257.

DISCUSSION OF RESULTS

The atomic polarization values found for fluorobenzene and chlorobenzene are slightly smaller than those usually found for polar molecules of this size[2] and that for nitrobenzene a little larger, but, in view of the large error necessarily accumulated in these quantities, particularly, in the value for nitrobenzene, the differences are not significant.

When the value 1.57 was obtained for the moment of fluorobenzene, it seemed surprisingly high in comparison with the values 1.39[3] and 1.45[4] previously found in benzene solution. The value 1.70 then found for chlorobenzene vapor was higher by a corresponding amount than the results of the more accurate determinations among the many which had been made in solution.[5] The precise determinations of Müller[6] upon very dilute solutions then showed that the apparent dipole moment of a molecule increased with decreasing dielectric constant of the surrounding solvent. The part of the polarization given by P_E is practically independent of solvent,[7] but the orientation polarization P_M due to the permanent dipole in the molecule is given, according to Müller, by the empirical equation, $P_{M\ \text{gas}}=P_{M\ \text{sol.}}/[1-0.075(\epsilon-1)^2]$, where ϵ is the dielectric constant of the solvent in which the orientation polarization at infinite dilution, $P_{M\ \text{sol.}}$, is determined. A similar equation gives the moment in the vapor state as $\mu_{\text{gas}}=\mu_{\text{sol.}}/[1-0.038(\epsilon-1)^2]$, no correction for atomic polarization being made in $P_{M\ \text{sol.}}$ and $\mu_{\text{sol.}}$. Although the polarization and moment values of the vapors of chlorobenzene and nitrobenzene were unknown to Müller, he showed that these equations represented their variations with solvent. Application of the second equation to the results of Bergmann and of Nukada gives a calculated value 1.55 for the moment of fluorobenzene in the vapor state in excellent

[2] C. P. Smyth, J. Chem. Phys. **1**, 247 (1933).
[3] P. Walden and O. Werner, Zeits. f. physik. Chemie **B2**, 10 (1929).
[4] E. Bergmann, L. Engel and S. Sandor, ibid. **B10**, 106 (1930); A. Nukada, Nia. Chem. **5**, 41 (1932).
[5] Cf. Trans. Faraday Soc., Appendix, September (1934).
[6] H. Müller, Phys. Zeits. **34**, 689 (1933).
[7] C. P. Smyth, E. W. Engel and E. B. Wilson, Jr., J. Am. Chem. Soc. **51**, 1736 (1929).

agreement with the observed value in Table II. As these equations take no account of the atomic polarization, for which Walden and Werner make an arbitrary correction in the calculation of the moment, the first empirical equation is applied to Walden and Werner's value for the total polarization minus a value 25 for P_E. The value $\mu_{gas}=1.54$ is thus obtained. Application of the first empirical equation to Müller's determinations of the polarization of chlorobenzene in nine different solvents and calculation of the moment from the resulting $P_{M\ gas}$ values give moment values for the vapor state running from 1.62 to 1.67 with a mean value 1.65, slightly lower than the observed value 1.70 in Table II, which is in excellent agreement with the value 1.69 recently published by Groves and Sugden[8] for the vapor. A similar calculation from Müller's results on nitrobenzene in various solvents gives 4.18, 4.21 and 4.22 for the values obtained from solutions in hexane, carbon tetrachloride and benzene, respectively, and 4.29 and 4.37 from dekaline and carbon bisulfide. Calculations from the results of Jenkins[9] give 4.14 from the dekaline solutions at 25° and 4.09 at 142.4° and 4.06 from carbon bisulfide solutions. The mean of the results from the data of the two investigators for each substance happens to be close to the values found from the work of both investigators on other solvents. Jenkins' measurements in chloroform solution, however, give a calculated value of 6.84 for the nitrobenzene moment in the gaseous state indicating either that the solvent has some specific action on the solute in this case or that the empirical equation cannot be relied upon when markedly polar solvents are used. The mean obtained from Müller's measurements in hexane, carbon tetrachloride and benzene is 4.20 and that from Jenkins' measurements in the same solvents and in cyclohexane is 4.18 in excellent agreement with the observed value 4.19 in Table II, which is in satisfactory agreement with the experimental value 4.23 recently published by Groves and Sugden.[8]

It is evident that, in the case of the three substances here studied, the empirical relation found by Müller between the apparent polarization and dipole moment of a substance in solution and the dielectric constant of the solvent serves admirably to calculate the moment in the vapor state. This added experimental evidence of the marked difference in some cases between the moment of the vapor and the apparent moment in solution emphasizes the need of considering the conditions under which moment values are determined before conclusions may be drawn from small differences in value. For instance, the difference in moment between chlorobenzene and methyl chloride[10] is only 0.16, while early work used a solution value for chlorobenzene to assign a value 0.4 to the difference. Since, however, most comparisons have been based upon measurements in the same solvent or in solvents differing by no great amount in dielectric constant, few, if any, of the accepted conclusions can be regarded as invalidated by this recent development.

[8] L. G. Groves and S. Sugden, J. Chem. Soc. 1094 (1934).
[9] H. O. Jenkins, Nature **133**, 106 (1934); Trans. Faraday Soc. **30**, 739 (1934).
[10] R. Sänger, Helv. Phys. Acta **3**, 161 (1930); O. Fuchs, Zeits. f. Physik **63**, 824 (1930).

LETTERS TO THE EDITOR

Bond Energies of the Hydrocarbons: Corrections Yielding Additivity

Zahn[1] has recently proposed an additional interaction energy between hydrocarbon bonds in order to account for the non-additivity of the bond energies of hydrocarbons. Some such treatment appears justified in view of the excellent data of Rossini[2] who has determined the heats of combustion of the normal aliphatic hydrocarbons with sufficient accuracy to detect deviations from additivity among the first members of the series. Also, to account for the existing data for other compounds, Pauling and Sherman[3] have proposed a resonance energy between certain isomeric configurations; for example, the two Kekulé structures of benzene.

In this note attention is directed to the possibility of attaining bond additivity by simply applying the following corrections: (1) Zero-point vibrational energy of each particular molecule; (2) a cross-interaction between the hydrogen atoms attached to the same carbon atom; (3) referring the heats of dissociation into atoms to 0°K. The results are in Table I. All energies are in kilocalories.

TABLE I.

	V_0'	ϵ_0	V_0 Exp.	Number of Bonds C−H	H..H	C−C	C=C	V_0 Calc.	Percent deviation
CH_4	356.7	27.3	384.0	4	6	0	0	384.0	——
C_2H_6	595.9	44.2	640.1	6	6	1	0	640.1	——
C_3H_8	837.4	61.7	899.1	8	7	2	0	899.2	+0.01
C_4H_{10}	1079.4	78.4	1157.8	10	8	3	0	1158.3	+0.04
C_5H_{12}	1321.3	96.6	1417.9	12	9	4	0	1417.4	−0.03
C_6H_{14}	1563.5	116.9	1680.4	14	10	5	0	1676.5	−0.23
C_7H_{16}	1805.7	135.1	1940.8	16	11	6	0	1935.6	−0.26
C_8H_{18}	2047.8	150.7	2198.5	18	12	7	0	2194.7	−0.17
C_2H_4	469.3	33.4	502.7	4	2	0	1	502.7	——
C_6H_6	1101.8	62.0	1163.8	6	0	3	3	1160.4	−0.28
				6	0	9	0	1206.9	+3.78
C_6H_{10}	1329.6	91.7	1421.3	10	4	5	1	1423.2	+0.13
C_6H_{12}	1451.1	111.0	1562.1	12	6	6	0	1554.6	−0.48

For the reaction $C_mH_n(g) \rightarrow mC(g) + nH(g)$ one need only consider the zero-point energy of the hydrocarbon, for that of the compounds used in the auxiliary chemical equations cancels. In calculating this energy for the aliphatic hydrocarbons the frequencies used are from Kohlrausch and Köppel,[4] and those for cyclohexane, cyclohexene and benzene are also from recent work.[5] This zero-point energy, $\epsilon_0 = \Sigma_i h\nu_i/2 = \Sigma_i [.00142\bar{\nu}_i(\text{cm}^{-1})]$ kcal. per mole is an appreciable factor, as shown from Table I. This energy is distributed over the whole molecule and cannot be said to reside in any particular bonds.

The value of 136.5 kcal. was used for the heat of vaporization of carbon. This figure was calculated from the recent work of Lozier,[6] who slightly favors this value over an alternate value of 182.0 kcal. However, the absolute value is not significant in this calculation; any reasonable value used consistently throughout would serve the same purpose. The heats of dissociation of H_2O into H_2 and O_2, of CO_2 into graphite and O_2, and of H_2 into hydrogen atoms were taken as 68.31, 94.24 and 102.9 kcal., respectively. The heats of combustion are from the work of Rossini[2] or from the table compiled by Kharasch. The corrections to 0°K were made for the hydrocarbons by the use of the same frequencies from which the zero-point energies were calculated. The change in heat content of the hydrogen atoms from 298° to 0°K was calculated. The uncertainties in the heat of vaporization of carbon are more than sufficient to absorb the correction of the carbons to 0°K. It turned out that the results were not very sensitive to these corrections to 0°K.

In Table I, V_0' is the heat of dissociation of the hydrocarbons into gaseous atoms at 0°K, and V_0 is the sum of ϵ_0 and V_0'. It is the sum that gives the total depth of the potential energy valley.

A cross-interaction between the hydrogens of 3.0 kcal. attraction is proposed. This is frankly an empirical correction factor. There are probably several ways of accounting for this value, perhaps the simplest being the predominating van der Waals energy of attraction. One need only consider the pairs of hydrogens attached to the same carbon atom, for the other hydrogens are too far removed from each other to contribute effectively.

Using the value of 3.0 kcal. attraction for H . . . . H, the C−H bond, as obtained from methane, equals 91.5 kcal.; the C−C bond, as obtained from ethane, equals 73.1 kcal.; the C=C bond, as obtained from ethylene, equals 130.7 kcal.

The first point to observe from an examination of Table I is that all of the aliphatic hydrocarbons have additive bond energies to within the accuracy of the data available. This accounts for the deviations reported by Rossini. The second and most important point is that benzene has a heat of dissociation equal to the sum of 6(C−H), 3(C−C) and 3(C=C) bonds. This suggests that it is not certain that resonance energy is as important as has been supposed. The data available are such as to make any final decision on this point premature. Finally, it is to be noted that cyclohexane and cyclohexene indicate further the consistency of this analysis.

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V. DEITZ*

University of Illinois,
Urbana, Illinois,
November 12, 1934.

* National Research Fellow.

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The Normal Frequencies of Vibration of the Plane Square Molecule AB_4 with Reference to the Structure of Nickel Carbonyl

Duncan and Murray[1] have recently studied the normal vibrations of the plane square molecule AB_4, using the method of mechanical models devised by Andrews.[2] They also applied their results to the interpretation of the Raman spectrum of $Ni(CO)_4$, considering the CO groups as dynamic units, and came to the conclusion that this molecule has the plane structure. Whereas it is certainly possible that this is the structure, I do not believe that their arguments in support of it are correct.

In the first place it seems very doubtful if any conclusions can be drawn by treating the CO groups as dynamic units, as they have done. Furthermore, it is unnecessary to do so, since the complete molecule can be treated by analytical methods without great difficulty. However, if we grant the validity of this approximation, their results are nevertheless incorrect because they did not take account of the selection rules[3] in the Raman effect. They correlated every mode of vibration of their models with an observed Raman line, whereas the vibrations ω_2, ω_3, ω_4 and ω_6 of their figure can be shown to be forbidden in the Raman effect. Their assignment of frequencies is consequently not valid and cannot therefore be used either directly as an argument for the plane structure or as a basis for the calculation of the symmetry number.

Although the model AB_4 is probably not a good approximation to $Ni(CO)_4$, it is so easy to treat analytically that I have done so and given the results below. The application of group theory leads to normal modes of vibration in agreement with those given by Duncan and Murray in Fig. 1 of their paper. The symmetry requirements[3b] also show that ω_1, ω_2, ω_5, ω_6 and ω_7 are obtainable from linear factors of the secular equation, while ω_3 and ω_4 are the roots of a quadratic factor.

The most general quadratic potential function for this model has eight independent force constants.[4] Since there is no way in which so many constants can be evaluated, the potential energy has been expressed in terms of the three constants K, H and h of stretching and bending of the valence bonds. Experience has shown that these are usually sufficient to give a rough fit of observed spectra and at present it is not certain which of the other constants are the most important.

$$\therefore 2V = K\sum_{i=1}^{4}\Delta R_i^2 + HR_0^2\sum_{i=1}^{4}\Delta\gamma_i^2 + hR_0^2\sum_{i=1}^{4}\Delta\beta_i^2.$$

ΔR_i is the extension of the bond $A-B_i$ from its equilibrium length, R_0, $\Delta\gamma_i$ is the angle of bending of the same bond in the plane of the molecule, and $\Delta\beta_i$ is the angle of bending of the ith bond out of this plane. K, H and h are the force constants.

This expression, by means of the methods previously described,[4] leads to the following formulas for the seven normal frequencies of vibration.

$$\lambda_1 = K/m,\ \lambda_2 = h/m,\ \lambda_5 = H/m,$$
$$\lambda_6 = (1+4m/M)h/m,\ \lambda_7 = K/m,$$
$$\lambda_{3,4} = (1/2m)\{(1+2m/M)(H+K) \pm [(1+2m/M)^2(H+K)^2 - 4(1+4m/M)KH]^{\frac{1}{2}}\},$$

where

$$\omega_i^2 = \lambda_i/4\pi^2C^2.$$

m, M are the masses of atoms B and A, respectively, in grams; c is the velocity of light, and ω is the frequency in wave numbers if K, H and h are in dynes per cm.

Except for the undesired effect of the masses of the springs, etc., these formulas should give the frequencies of the mechanical models when the proper values are inserted for K, H and h. Since it is a matter of a few hours at most to obtain these formulas and since they permit the variation of the force constants whereas the mechanical models require new springs for every such change, the analytical method seems to me very much simpler and more useful than the model method, at least for such symmetrical molecules.

The complete nine-atom model of $Ni(CO)_4$ is now being treated analytically. The number of fundamental frequencies which may appear in the Raman, the infrared, and in both spectra for this complete model are listed in Table I for the two configurations. Definite conclusions

TABLE I. *Selection rules for fundamental frequencies of $Ni(CO)_4$.*

No. of frequencies	Raman active	Infrared active	Active in both	Inactive
Plane	7	6	0	3
Tetrahedron	8	4	4	1

regarding the structure will require a careful comparison of the infrared and Raman lines in terms of the formulas for the normal frequencies. Frequencies listed in the third column are also enumerated in the first two columns.

E. BRIGHT WILSON, JR.*
Mallinckrodt Chemical Laboratory,
Harvard University,
November 15, 1934.

* Junior Fellow of the Society of Fellows.

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The Raman Spectrum of 1,3-Cyclohexadiene

In order to study the changes in the Raman spectrum which accompany the progressive introduction of double bonds into the cyclohexane ring, the Raman spectrum of 1,3-cyclohexadiene has been investigated. The Raman spectra of cyclohexane, cyclohexene, and benzene are well known, and 1,3-cyclohexadiene constitutes a hitherto missing member of this interesting series of spectra. The material used was prepared from cyclohexene by the method described by Crossley.[1] The sample was fractionated several times with a small column and boiled at 80–81°C. The technique employed to obtain the spectrum was that described by Murray and Andrews.[2] Spectra were excited by the 4358 and 4046 mercury lines separately using filters.

The following Raman frequencies were found: 298(4), 394(2), 458(1), 505(0), 559(1), 618(1), 823(10), 848(8), 945(4b), 992(15), 1060(2), 1174(4), 1220(3), 1240(2), 1266(1), 1324(1), 1411(1), 1432(5), 1576(20), 1615(3), 2823(8b), 2864(8b), 2908(4), 2936(8), 3018(5), 3041(10), 3056(7). The figures given in parentheses are visually estimated relative intensities.

The chemical behavior of 1,3-cyclohexadiene is very different from that of benzene or that of cyclohexane as there are two double bonds of distinctly ethylenic character. In view of this fact, it is interesting to note that most of the strong lines in the benzene spectrum have counterparts in the spectrum of 1,3-cyclohexadiene. Because of the lower symmetry, there are more strong lines in the latter spectrum, the number being nearly the same as in the spectrum of cyclohexene which has the same degree of symmetry. The low frequency line at 176 in cyclohexene is not found in the spectrum of 1,3-cyclohexadiene. Two lines are found in this spectrum in the region associated with double bond vibrations both of which have lower frequencies than the lines in this region of the cyclohexene spectrum and are rather close to the positions of the benzene lines in this region. This appears to support the assignments of these benzene lines to vibrations involving double bonds.

JOHN W. MURRAY
Chemistry Laboratory,
The Johns Hopkins University,
November 26, 1934.

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The Oxidation of Fe^{++} to Fe^{+++} by the Irradiation with X-Rays of Solutions of Ferrous Sulfate in Sulfuric Acid

In earlier work[1] we have studied the chemical effect of x-rays on ferrous sulfate in 0.8N sulfuric acid. This work has now been extended by a study of the influence of the hydrogen ion in this reaction. Solutions of ferrous sulfate in sulfuric acid, gas-free or containing oxygen at different pressures, were irradiated and analyzed for the ferrous ion, hydrogen and oxygen. The temperature was 30°C. For the wavelength used, the x-ray absorption for all irradiated solutions was practically the same as for water. The ferrous ion concentration was determined by electrometric titration with potassium dichromate. Analysis for hydrogen and oxygen was made by means of a van Slyke apparatus.

In gas-free solutions, hydrogen is produced, the number of moles being slightly larger than one-half the number of ferrous ions oxidized. In solutions containing oxygen, none, or a very small quantity of hydrogen is produced. The number of moles of oxygen consumed is slightly less than one-fourth the number of ferrous ions oxidized. The lack of exact equivalence may be due to the action of the rays on traces of organic impurities in the solutions, resulting in the production of a small quantity of hydrogen and the binding of a small quantity of oxygen.

The number of ferrous ions oxidized per unit of dosage depends on the hydrogen ion concentration, and is within certain limits independent of the concentration of the ferrous and the sulfate ions, and, for solutions containing oxygen, of the oxygen pressure. The ferrous ion concentration has been changed from 50 micromoles per liter to such concentrations as can be obtained in solution, but not over one millimole per liter. In the earlier work[1] at pH equal to 0.5, the independence was established up to 10.0 millimoles per liter of ferrous sulfate. The oxygen pressure has been changed from 70 to 1 cm of mercury. The sulfate ion concentration has been varied by the addition of sodium sulfate in concentrations up to 0.4 molar. The results obtained show that the oxidation of the ferrous ion is due to a primary activation of the water by the x-rays.

The dependence on the hydrogen ion concentration is shown in Fig. 1, where the number of microequivalents of

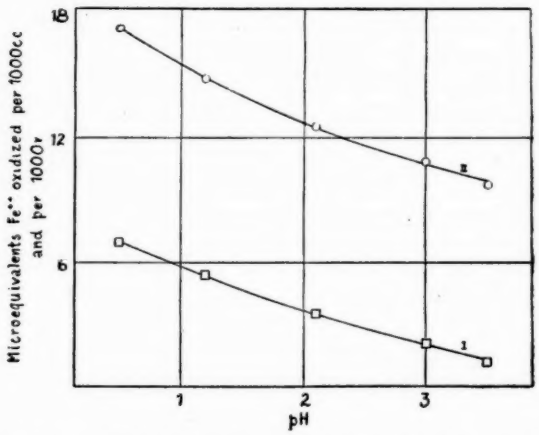

FIG. 1. The oxidation of ferrous sulfate in sulfuric acid as a function of the pH of the irradiated solution. I. gas free; II. oxygen present.

ferrous ion oxidized per 1000 cc of solution and per 1000 r of dosage is given as a function of the pH, for gas-free solutions (I) and for solutions containing oxygen (II). The two curves have a constant difference of 8.8 microequivalents.

The reaction occurring in gas-free solution may be written:

$$Fe^{++}+H^{+}=Fe^{+++}+\tfrac{1}{2}H_2. \qquad (1a)$$

In solutions containing oxygen, it would appear that this same reaction occurs, but the hydrogen evolved is oxidized to water in a secondary reaction, giving as the complete reaction:

$$Fe^{++}+H^{+}+\tfrac{1}{4}O_2=Fe^{+++}+\tfrac{1}{2}H_2O. \qquad (2a)$$

Furthermore, the additional reaction, which is independent of the pH, takes place:

$$Fe^{++}+\tfrac{1}{4}O_2+\tfrac{1}{2}H_2O=Fe^{+++}+OH^{-}, \qquad (2b)$$

this reaction being represented by the difference between curves I and II. The continuous rise of curve I is rather

surprising, since reaction (1a) is endothermic. Unfortunately, it is not feasible to extend the measurements below the range of pH used.

HUGO FRICKE
EDWIN J. HART
The Walter B. James Laboratory for Biophysics,
The Biological Laboratory,
Cold Spring Harbor, Long Island, New York,
December 7, 1934.

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A New Approximation Method in the Problem of Many Electrons

The principles of an approximation method have been recently published by the author for systems consisting of closed shells and of valence electrons.[1] The method consists in treating simultaneously the atom kernels according to Thomas-Fermi and the valence electrons according to Schroedinger. It is possible to obtain an approximated Schroedinger equation for the valence electrons from the variation principle for the whole energy. There are no additional exclusion conditions for the valence electrons, arising from the states occupied by paired electrons. But the potential field for the valence electrons contains, besides the familiar electrostatic action of the charge of closed shells on the valence electrons, an additive term of the form $\partial T/\partial\rho$, where T is the kinetic energy per unit of volume of the paired electrons, ρ their density. (The theory of Thomas-Fermi gives $\partial T/\partial\rho=(h^2/8m)[(3/\pi)\rho]^{2/3}$.)

There is nothing to prevent the use of better distributions of electrical density ρ than those obtained from the Thomas-Fermi method. But even the use of the latter gives the right order of magnitude, e.g., for a univalent ion the potential function is, in the region from $r=\infty$ to $r=r_0(=4.6\text{A})$, the pure Coulomb potential, i.e., $-e^2/r$, and then the value $eV+\partial T/\partial\rho$ is constant, being equal to $-e^2/r_0$.[2] If we put the valence electron into this potential hole, then its energy will be somewhat higher than the potential $-e^2/r_0$ at the bottom of the hole, namely, -3.1 volts. For caesium, where the application of the Thomas-Fermi solutions for the atomic kernels is better justified than in other cases, the experimental value is -3.9 volts. Without an additive potential and without the exclusion principle the valence electron would fall into the K-shell with many thousand volts of ionization energy.

The practical value of the method lies in that it allows us to obtain the entire potential function $eV+\partial T/\partial\rho$ from experimental data. The potential field and the corresponding eigenfunctions of the valence electrons can be obtained from the spectra so that the lowest state of the valence electrons corresponds to the lowest level obtained in the potential field without any additional conditions. These data enable us to enter upon the problem of boundary. Thus both the electrostatic and the exclusion principle influences of the atomic kernels on all the valence electrons are taken into consideration and the Ritz method may be used for the valence electrons alone.

For potassium a preliminary calculation suggested the expression $-1/r+(2.74/r)e^{-1.16r}$ for the complete potential for the valence electron, and the corresponding eigenfunction $\psi\sim e^{-0.29r}$ (approximated by means of the Ritz method expressed in atomic units). Then the Heitler-London method will give for K_2 an equilibrium distance of about 4A (exp.: 3.9A) and an energy of about 37 percent of the experimental value. It is this result which agrees very well with the results obtained by James[3] for Li_2 who considered the effects produced by closed shells in detail. We must also assume, that the greater part of the binding energy appears first in higher approximations. The accordance of the results of Rosen and Ikehara[4] and of others with experimental data must be ascribed to their being arbitrary assumptions. The decrease in the value of the triplet under the influence of the closed shells, emphasized by James, comes quite naturally in our calculation, for the additional potential changes not only the Coulomb interaction but also the exchange integrals. A diminution in the exchange integrals produces an increase in the singlet and a decrease in the triplet term. However, our having obtained more favorable results than may have been expected from James's calculations may be explained first by our having omitted the mutual interaction between atomic kernels and, secondly, by our having partially included the polarization forces with the closed shells in our empirical potential function.

For KH a rough approximation including, however, the homopolar and ionic states gives an equilibrium distance of about 2A and an energy of -0.8 volt. The share of the ionic state in the molecule is 80 percent. The difference as compared with the experimental value of -2.06 volts must be again explained by polarization forces. In the extreme case of pure ionic binding we can avail ourselves of the result of Hylleraas[5] for the internal polarization interaction of H^-. Then, in the subsequent calculation, only the resulting density (not the eigenfunctions) of the H^- atom plays a part. This was assumed approximately as $\sim e^{-11r/8}$. Thus we find an equilibrium distance of 1.9A and a binding energy of 1.95 volts.

A detailed account of the subject will shortly appear in the *Acta Physicochimica U. R. S. S.* The approximation method is being further elaborated for the alkaline molecules and its hydrides in this institute. The method shall be extended for polyvalent atoms.

H. HELLMANN
Karpow-Institute for Physical Chemistry,
Moscow,
November 26, 1934.

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